PB85-156180

Evaluation of At-Sea Disposal of FGC (Flue Gas Cleaning) Wastes. Volume 1 Biological Testing and Studies with Untreated Wastes

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 84

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/7-85-001a
December 1984
PB85-156180

EVALUATION OF AT-SEA DISPOSAL OF FGC WASTES:

Volume 1. BIOLOGICAL TESTING AND STUDIES WITH UNTREATED WASTES

C.B. Cooper, R.R. Lunt, I. Bodek

Arthur D. Little, Inc.
Acorn Park
Cambridge, MA 02140

Contract No. 68-03-2334

EPA Project Officer:

Julian W. Jones
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA Form 2350-4 (4-80)
(PREVIOUSLY EIN: EPA FORM 387)

TYPING GUIDE SHEET

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/7-85-001a

2.

3. RECIPIENT'S ACCESSION NO.
PB85 156180 /AS

4. TITLE AND SUBTITLE
Evaluation of At-sea Disposal of FGC Wastes: Vol. 1. Biological Testing and Studies with Untreated Wastes

5. REPORT DATE
December 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
C.B. Cooper, R.R. Lunt, I. Bodek, and C.J. Santhanam

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts 02140

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-03-2334

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Phase 3, Final; 5/77 - 10/83

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Julian W. Jones, Mail Drop 61, 919/541-2489. EPA-600/7-77-051 and -600/7-84-005 are related reports (Phases 1 and 2).

16. ABSTRACT

This two-part report is the third of a series on a continuing EPA research program on the feasibility of disposing of flue gas cleaning (FGC) wastes in the ocean. Part 1 gives results of laboratory-scale chemical and biological experiments with untreated (unstabilized) FGC wastes designed to provide basic data on environmental impact potential. Part 2 gives results of further chemical and biological tests with a forced-oxidation (sulfate-rich) FGC waste and with stabilized FGC wastes. Results of tests performed to date and related assessment efforts indicate that the conventional (concentrated-dump) at-sea disposal of unstabilized FGC wastes with soil-like properties on the Continental Shelf appears to be environmentally undesirable, unless contradicted by further work. Test results also indicate that at-sea dispersed disposal of sulfate-rich (and, possibly, sulfite-rich) soil-like FGC wastes is sufficiently promising to merit further research. Likewise, results of this and other programs indicate that conventional or concentrated disposal of brick-like stabilized FGC wastes is also promising.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Fly Ash	Pollution Control	13B
Flue Gases		Stationary Sources	21B
Gas Scrubbing		Flue Gas Cleaning	07A,13H
Waste Disposal			
Ocean Environments			08J
Assessments			14B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 167
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This is Part One of the third in a series of reports on a continuing research program sponsored by the U.S. Environmental Protection Agency on the feasibility of the disposal of Flue Gas Cleaning (FGC) wastes in the ocean. This part of the report presents the results of laboratory-scale chemical and biological experiments with untreated (unstabilized) FGC wastes designed to provide basic data on environmental impact potential. The testing was performed by Arthur D. Little, Inc. and the Edgerton Research Laboratory of the New England Aquarium. Part Two of this report presents the results of further chemical and biological testing with a forced-oxidation (sulfate-rich) FGC wastes and with stabilized FGC wastes.

The results of testing performed to data and related assessment efforts indicate that the conventional (concentrated-dump) ocean disposal of unstabilized FGC wastes with soil-like properties on the continental shelf appears to be environmentally undesirable unless contradicted by further work. Concentrated-dump disposal offers potential adverse physical impacts with regard to benthic sedimentation and descending waste masses in the ocean. Such disposal of unstabilized, sulfite-rich FGC wastes may result in oxygen depletion and consequent toxicity impacts.

Dispersed disposal of various FGC wastes and concentrated disposal of stabilized (brick-like) FGC wastes remain promising and worthy of further research.

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)

TYPING GUIDE SHEET

TABLE OF CONTENTS

Page

LIST OF TABLES vii

LIST OF FIGURES viii

ACKNOWLEDGEMENTS ix

CONVERSION FACTORS x

GLOSSARY xi

ABBREVIATIONS xii

I. SUMMARY 1
  A. BACKGROUND 1
  B. PURPOSE AND SCOPE 2
  C. RESULTS 2
  D. CONCLUSIONS 5
  E. RECOMMENDATIONS FOR ADDITIONAL RESEARCH 5
  F. REFERENCES 6

II. INTRODUCTION AND BACKGROUND 7
  A. OVERVIEW 7
  B. INITIAL ASSESSMENT 7
  C. REFINED ASSESSMENT 10
  D. PURPOSE, SCOPE AND APPROACH OF THIS PHASE 12

III. BIOLOGICAL TESTING 15
  A. ACUTE TOXICITY STUDIES WITH UNSTABILIZED FGC WASTES 15
  B. THIRTY-DAY EXPOSURE STUDIES WITH UNSTABILIZED FGC WASTES 22

TABLE OF CONTENTS
(Continued)

Page

IV. SUMMARY EVALUATION OF ENVIRONMENTAL IMPACT POTENTIALS 61

- A. BENTHIC SEDIMENTATION IMPACTS 61
- B. SUSPENDED SEDIMENT IMPACTS 61
- C. SULFITE-RELATED OXYGEN DEPLETION 62
- D. TRACE CONTAMINANT IMPACTS 62

V. CONCLUSIONS 64

VI. RECOMMENDATIONS FOR ADDITIONAL RESEARCH 65

VII. REFERENCES 66

Appendix A: Acute Toxicity Testing A-1

Appendix B: Long-Term Exposure Testing B-1

LIST OF TABLES

PAGE

TABLE 1 ANIMAL MORTALITY RECORD - LONG-TERM EXPOSURE TEST 4

TABLE 2 FGC WASTE SAMPLES USED IN LABORATORY TESTING 14

TABLE 3 MAJOR CONSTITUENTS OF FGC WASTE SAMPLES USED IN ACUTE TOXICITY TESTING 16

TABLE 4 96-HOUR BIOASSAY RESULTS 18

TABLE 5 MAJOR AND TRACE COMPOSITION OF WASTE SAMPLES TESTED 23

TABLE 6 EXPERIMENTAL PARAMETERS USED IN QUIESCENT LEACHING TESTS 27

TABLE 7 LONG-TERM EXPOSURE TESTS - WASTE CONTENT 31

TABLE 8 TRACE ELEMENT CONCENTRATIONS USED IN LONG-TERM TOXICITY TESTS 32

TABLE 9 RELEASE OF TRACE ELEMENTS FROM FGD WASTES INTO SEAWATER (μg/ℓ) UNDER STIRRED CONDITIONS 40

TABLE 10 COMPARISON BETWEEN AMOUNT OF TRACE ELEMENTS RELEASED TO SEAWATER IN STIRRED EXPERIMENT AND THAT PRESENT IN THE SOLIDS 41

TABLE 11 CONCENTRATIONS OF SELECTED TRACE ELEMENTS IN SEAWATER AFTER MIXING WITH FGD WASTE FOR SEVEN DAYS 42

TABLE 12 LEACHING DATA FOR FGD WASTES UNDER QUIESCENT CONDITIONS 43

TABLE 13 COMPARISON OF DATA FROM STIRRED VERSUS QUIESCENT LEACHING EXPERIMENTS 44

TABLE 14 CALCULATED THICKNESS OF FGD WASTE LAYER LEACHED DURING QUIESCENT EXPERIMENTS 49

TABLE 15 ANIMAL MORTALITY RECORD - LONG-TERM EXPOSURE TEST 50

LIST OF FIGURES

Page

FIGURE 1 48-HOUR BIOASSAY 21

FIGURE 2 EXPERIMENTAL SETUP FOR QUIESCENT LEACHING TEST 26

FIGURE 3 THIRTY-DAY EXPOSURE TANKS SETUP 29

FIGURE 4 STIRRED EXPERIMENT - SELENIUM RELEASED OVER TIME 34

FIGURE 5 STIRRED EXPERIMENT - NICKEL RELEASED OVER TIME 35

FIGURE 6 STIRRED EXPERIMENT - ZINC RELEASED OVER TIME 36

FIGURE 7 STIRRED EXPERIMENT - CADMIUM RELEASED OVER TIME 37

FIGURE 8 QUIESCENT LEACHING EXPERIMENTS - TOTAL SELENIUM RELEASED FROM THREE DIFFERENT WASTE HEIGHTS - LS-3 WASTE WITH TIME 38

FIGURE 9 QUIESCENT LEACHING EXPERIMENTS - TOTAL CADMIUM RELEASED FROM THREE DIFFERENT WASTE HEIGHTS - LS-3 WASTE WITH TIME 39

FIGURE 10 QUIESCENT LEACHING EXPERIMENT - TOTAL CADMIUM RELEASED FROM L-1 WASTE WITH TIME 45

FIGURE 11 QUIESCENT LEACHING EXPERIMENT - TOTAL NICKEL RELEASED FROM L-1 WASTE WITH TIME 46

FIGURE 12 QUIESCENT LEACHING EXPERIMENT - TOTAL SELENIUM RELEASED FROM L-1 WASTE WITH TIME 47

FIGURE 13 COMPARISON OF CADMIUM IN WASTES, WATER COLUMN, AND ORGANISM TISSUES 53

FIGURE 14 INCREASE IN CADMIUM IN CLAM TISSUE IN THIRTY-DAY TEST WITH L-1 WASTE 55

FIGURE 15 COMPARISON OF NICKEL IN WASTES, WATER COLUMN, AND ORGANISM TISSUES 56

FIGURE 16 COMPARISON OF SELENIUM IN WASTES, WATER COLUMN, AND ORGANISM TISSUES 58

FIGURE 17 COMPARISON OF ZINC IN WASTES, WATER COLUMN, AND ORGANISM TISSUES 60

ACKNOWLEDGEMENTS - PART ONE

This study was conducted by Arthur D. Little, Inc. for the U.S. Environmental Protection Agency under Contract No. 68-03-2334. The Edgerton Research Laboratory of the New England Aquarium (NEA) performed the biological testing under subcontract to Arthur D. Little, Inc.

This report reflects the work of many members of Arthur D. Little, Inc. and the NEA staff. Those participating in this phase of the program are listed below.

Arthur D. Little, Inc.	Edgerton Research Laboratory New England Aquarium
Principal Investigators:	
Richard R. Lunt	Guy C. McLeod, Laboratory Director
Charles B. Cooper	Albert J. Barker
Itamar Bodek	Thomas R. Gilbert
Contributing Staff:	
Rena S. Glickman	Alice Clay
James R. Valentine	Kathleen Smith
	G. Stacey

Many other individuals and organizations have made contributions to this study. In particular, we wish to acknowledge the continuing assistance and guidance provided by Julian W. Jones, the EPA Project Officer, throughout the course of this program. We would also like to thank the utility companies which supplied FGC waste samples used in the testing.

CONVERSION FACTORS

English/American Units	Metric Equivalent
Length:	
1 inch	2.540 centimeters
1 foot	0.3048 meters
1 fathom	1.829 meters
1 mile (statute)	1.609 kilometers
1 mile (nautical)	1.852 kilometers
Area:	
1 square foot	0.0929 square meters
1 acre	4,047 square meters
Volume:	
1 cubic foot	28.316 liters
1 cubic yard	0.7641 cubic meters
1 gallon	3.785 liters
Weight/Mass:	
1 pound	0.4536 kilograms
1 ton (short)	0.9072 metric tons
Pressure:	
1 pound per square inch	0.07031 kilograms per square centimeter
Concentration:	
1 part per million (weight)	1 milligram per liter
Speed:	
1 knot	1.853 kilometers per hour
Energy/Power:	
1 British Thermal Unit	1,054.8 joules
1 megawatt	3.600 x 10^9 joules per hour
Δ Temperature:	
1 degree Fahrenheit	5/9 degree Centrigrade

GLOSSARY

Cementitious: A chemically precipitated binding of particles resulting in the formation of a solid mass.

Fixation: The process of putting into a stable or unalterable form.

Impoundment: Reservoir, pond, or area used to retain, confine, or accumulate a fluid material.

Leachate: Soluble constituents removed from a substance by the action of a percolating liquid.

Leaching Agent: A liquid used to percolate through a substance that results in the leaching of soluble constituents.

Pozzolan: A siliceous or aluminosiliceous material that in itself possess little or no cementitious value but that in finely divided form and in the presence of moisture will react with alkali or alkaline earth hydroxide to form compounds possessing cementitious properties.

Pozzolanic Reaction: A reaction producing a pozzolanic product.

Stabilization: Making stable by physical or chemical treatment.

ABBREVIATIONS

Btu	British thermal unit
cm	centimeter
cm/sec	centimeter per second
^oC	degrees Centigrade
^oF	degrees Fahrenheit
ESP	electrostatic precipitator
FGC	flue gas cleaning
FGD	flue gas desulfurization
ft	feet
ft/sec	feet per second
g	gram
gal	gallon
gpm	gallons per minute
hp	horsepower
hr	hour
in.	inch
j	joule
j/s	joule per second
k	thousand
kg	kilogram
km	kilometer
kW	kilowatt
kWh	kilowatthour
l	liter
lb	pound
M	million
m^2	square meter
m^3	cubic meter
Mw	megawatt
ppm	parts per million
psi	pounds per square inch
sec	second
TDS	total dissolved solids

Note: For conversion units, see page viii.

I. SUMMARY

A. BACKGROUND

This is Part One of the third in a series of reports on a research program sponsored by the U.S. Environmental Protection Agency on the feasibility of disposal of Flue-Gas Cleaning (FGC) wastes from coal-fired power plants in mines and at sea. The previous two reports (1)(2) presented findings concerning both mine and ocean disposal. The initial study (1) consisted of issue identification for future research, based eased on review of available information. The report on the second phase of work (2) included the results of original physical and chemical testing as well as additional assessment of available literature. This report, presented in two parts, describes the subsequent investigations of ocean disposal by Arthur D. Little, Inc. (ADL) and the Edgerton Research Laboratory of the New England Aquarium (NEA). A separate report covers the further investigations of mine disposal.

Initial studies in this program (1) identified four environmental impact categories of concern in the potential at-sea disposal of FGC wastes from coal-fired power plants. These categories were:

- benthic sedimentation;
- suspended waste in the water column;
- sulfite-related toxicity and oxygen depletion; and
- trace contaminants.

The second phase of the program (2) focused on physical and chemical investigations of unstabilized FGC wastes in seawater. Testing and assessment efforts emphasized three subject areas:

- physical fate of unstabilized FGC wastes in the water column;
- physical fate of unstabilized FGC wastes on the ocean bottom; and
- chemical fate of unstabilized FGC wastes in seawater.

Overall conclusions of the first two phases emphasized the need for case-by-case analyses of prospective at-sea disposal of FGC wastes, along with the following more specific conclusions:

- The conventional disposal of unstabilized FGC wastes with soil-like physical properties on the continental shelf appeared to be environmentally undesirable without further, contradictory evidence.
- Problems of at-sea disposal of sulfite-rich FGC wastes, particularly those related to oxygen depletion, appeared to be

much greater than the problems associated with other FGC wastes.

- Disposal options which appeared promising and worthy of further research included:
  - dispersed disposal of unstabilized sulfate-rich and stabilized brick-like FGC wastes on the continental shelf;
  - concentrated disposal of brick-like FGC wastes; and
  - disposal of unstabilized sulfate-rich FGC wastes in the deep ocean.

B. PURPOSE AND SCOPE

This third phase of the program was designed to fulfill several research needs identified in the earlier assessments. Experiments were designed to study:

1. acute toxicity of unstabilized FGC wastes to marine water column organisms;
2. chronic toxicity and substrate suitability of unstabilized FGC wastes for marine benthic organisms; and
3. leaching behavior and bioaccumulation of trace contaminants from FGC wastes in seawater.

One series of tests consisted of measurements of the acute toxicity of unstabilized FGC wastes to marine zooplankton and finfish, with the wastes maintained in suspension in the water column. The second series of tests was conducted in two parts. First, leaching tests were conducted to determine the amounts of selected metallic trace contaminants that could leach from the wastes under different mixing conditions. Then, six-week exposure tests were performed in flow-through seawater systems with partial FGC waste substrates and marine benthic plants, invertebrates, and finfish. Organisms and the water column were monitored for the trace metals for the duration of the tests.

C. RESULTS

1. Suspended Sediment Impacts

The results of toxicity testing with suspended wastes and water-column organisms indicated that there are unlikely to be significant differences between the water column impacts of descending, sulfate-rich FGC wastes and impacts presently experienced in disposal of dredged materials. Specifically, test results were obtained for marine/estuarine species with documented high sensitivity to suspended sediment impacts, i.e., the zooplankter *Acartia tonsa* and the filter-feeding fish *Menidia menidia*. The toxicity values upon exposure of these species to suspended sulfate-rich, soil-like FGC wastes were in the same range as those obtained by other investigators(3) upon exposure of the same species to suspensions of various natural soils under comparable test conditions.

However, exposure of the same species to agitated suspensions of sulfite-rich, unstabilized FGC wastes produced dramatic oxygen depletion and organism mortality. The latter results suggest that conventional release of descending masses of unstabilized, sulfite-rich FGC wastes could lead to toxic phenomena in the ocean water column, depending on the degree of attraction to or voluntary avoidance of the descending masses by disposal site organisms. Dispersed, rather than conventional disposal of these wastes, or disposal following stabilization, are possible means of mitigating this impact potential.

2. Sulfite-Related Oxygen Depletion on the Ocean Bottom

The results of month-long exposure tests with benthic marine organisms reinforced earlier concerns over the potential adverse effects of sulfite-related oxygen depletion. In circumstances where unstabilized, sulfite-rich FGC wastes comprised one-fourth or more of the test tank substrate, finfish agitated the wastes sufficiently to lead to oxygen depletion and organism mortality. However, in circumstances where the wastes comprised smaller areas of the tank substrate, voluntary avoidance and an absence of oxygen depletion and organism mortality prevailed throughout the tests.

These results suggest that dispersed disposal combined with voluntary avoidance may provide means of mitigating the oxygen-depletion impact potential of unstabilized, sulfite-rich FGC wastes, but field-scale observations would be needed to evaluate this possibility.

3. Trace Contaminant Impacts

The results of the exposure tests concerning leaching, toxicity and bioaccumulation of trace metals varied for the several chemicals and wastes investigated. As illustrated in Table 1, the exposure conditions associated with one unstabilized, sulfate-rich waste resulted in extensive mortality of experimental invertebrates (clams and snails), but had no comparable effect on finfish (flounder). There was no apparent explanation for the observed toxicity of this one sulfate-rich waste, as the measured levels of trace metals in the water column were within the non-toxic range observed by other researchers working with other comparable metal mixtures and the same marine organisms(4)(5). Possible explanations included the presence of high levels of an unmeasured chemical (i.e., copper) or the contamination of the waste sample in some other manner not detectable by traditional bulk or trace metal analysis.

There was an absence of toxicity and significant bioaccumulation associated with the leaching of nickel and zinc in tests with FGC wastes relatively rich in these constituents (compared with the full range of data on other FGC wastes(6)). This result suggested that the levels of nickel and zinc, two trace contaminants identified as

TABLE 1

ANIMAL MORTALITY RECORD
LONG-TERM EXPOSURE TEST

Date	Number	Organism	Tank No.	Waste
July 3	2	Psuedopleurenectes	1	Control
	1	Littorina	8	Control
July 5	1	Mya	6	LS3
	1	Littorina	6	LS3
July 6	4	Mya	6	LS3
July 7	1	Mya	6	LS3
	2	Littorina	6	LS3
July 8	1	Mya	6	LS3
July 11	1	Littorina	5	DA1
July 12	1	Littorina	5	DA1
	3	Littorina	6	LS3
July 20	2	Littorina	6	LS3
	1	Littorina	8	Control
July 21	1	Mya	6	LS3
	1	Mya	overflow tank	LS3
July 24	1	Littorina	6	LS3
	1	Littorina	8	Control
July 25	2	Mya	overflow tank	LS3
July 26	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
July 27	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
August 7	1	Mya	overflow tank	LS3

SOURCE: New England Aquarium.

potential problems in the earlier work, would be unlikely to preclude ocean disposal of FGC wastes.

Results for cadmium and selenium indicated continuing release and bioaccumulation of these chemicals upon testing with some of the experimental FGC wastes in seawater. These results indicated that further testing of FGC wastes relatively rich in these metals would be required to evaluate fully their long-term impact potential.

D. CONCLUSIONS

Overall conclusions regarding the need for case-by-case disposal evaluations and the technical feasibility of control options were still considered valid. Other specific conclusions were, in summary:

- The concentrated disposal at-sea of unstabilized FGC waste with soil-like physical properties still appears to be environmentally undesirable, unless contradicted by further work.
- The problems of disposal of sulfite-rich FGC wastes still appear considerable, but dispersal appears to be a potentially useful control option.
- The potential release of some trace contaminants remains a valid concern that could preclude at-sea disposal of FGC wastes. This concern does not appear to extend to nickel and zinc.
- Dispersed disposal at-sea of all forms of FGC wastes and concentrated disposal at-sea of stabilized brick-like FGC wastes appear promising and are recommended for further research.
- Conventional disposal of unstabilized sulfate-rich FGC wastes in the deep ocean may be promising, but needs to be reconsidered after further testing to determine if the toxicity of one such waste in this program was an isolated phenomenon.

E. RECOMMENDATIONS

The more important research needs identified from these investigations were:

- further bioassay data on sulfate-rich FGC wastes;
- further leaching and bioassay data on selected FGC waste trace contaminants;
- limited field-scale tests to investigate avoidance responses and trace contaminant uptake;
- parallel data for stabilized FGC wastes; and

- continued investigations of any full-scale field situations where FGC wastes have entered or been placed in marine environments.

F. REFERENCES

1. Lunt, R.R., C.B. Cooper, S.L. Johnson, J.E. Oberholtzer, G.R. Schimke, and W.I. Watson, "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," EPA 600/7-77-051, U.S. Environmental Protection Agency, Office of Research and Development, 1977.

2. Lunt, R.R., C.B. Cooper, A.S. Reyman, S.L. Johnson, I. Bodek, W.I. Watson, (Arthur D. Little, Inc.) and G.C. McLeod, A.J. Barker, (Edgerton Research Laboratory, New England Aquarium), "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Refined Assessment." Report to U.S. Environmental Protection Agency, Office of Research and Development under Contract No. 68-03-2334, 1981.

3. Sherk, J.A., J.S. O'Connor, and D. Neumann, "Effects of Suspended and Deposited Sediments on Estuarine Organisms, Phase II." Final Report, University of Maryland, Department of Environmental Research, Chesapeake Biological Laboratory, 1974.

4. Eisler, Ronald and Raymond J. Hennekey, "Acute Toxicities of Cd^{2+}, Cr^{+6}, Hg^{2+}, Ni^{2+}, and Zn^{2+} to Estuarine Macrofauna," EPA-600/J-77-151, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 19877.

5. Eisler, Ronald and Raymond J. Hennekey, "Toxicity Evaluation of a Complex Metal Mixture to the Soft Shell Clam (*Mya arenaria*)," EPA-600/J-77-149, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

6. Santhanam, C.J., R.R. Lunt, C.B. Cooper, D.E. Kleinschmidt, I. Bodek, W.A. Tucker (Arthur D. Little, Inc.), and C.R. Ullrich (University of Louisville), "Waste and Water Management for Conventional Coal Combustion, Assessment Report - 1979," EPA 600/7-80-012, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, 1980.

II. INTRODUCTION

A. OVERVIEW

This is Part One of the third of a series of reports on a continuing research program sponsored by the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency. The program consists of investigations by Arthur D. Little, Inc., the Edgerton Research Laboratory of the New England Aquarium, and various other organizations of the feasibility of disposal, in mines and at-sea, of flue gas cleaning (FGC) wastes from utility coal combustion. Previous reports in this series summarized the results of theoretical, laboratory, and limited field-scale evaluations. This part of the report focuses on the results of a series of laboratory-scale chemical and biological experiments with untreated (unstabilized) FGC wastes designed to provide information on the environmental feasibility of disposal of such wastes at-sea. It also summarizes the results of all the theoretical and experimental studies of disposal of untreated wastes in the program. The results of continuing investigations of the feasibility of FGC waste disposal in coal mines are discussed in a separate, parallel report. Further investigations, reported in Part Two, focused on the feasibility of disposal of treated (chemically stabilized) FGC wastes at-sea.

B. INITIAL ASSESSMENT

The rationale for the experimental work documented in this report emerged from the findings of the two previous investigative phases of this program. The first phase, the "Initial Assessment" (1), was theoretical (rather than experimental) in nature and consisted of an issue identification process based on assembly and review of existing information. The information reviewed included the findings of many researchers concerning the environmental effects of various ocean disposal activities, and the findings concerning important physical and chemical characteristics of FGC wastes. Four principal categories of potential environmental impacts and three aspects of the then-extant regulatory framework were identified as significant issues. The four environmental impact categories of concern were:

- benthic sedimentation;
- suspended waste in the water column;
- sulfite-related toxicity and oxygen depletion; and
- trace contaminants.

The three aspects of the regulatory framework judged to be of special significance at that time were:

- definitions of limiting permissible concentrations in disposal area "mixing zones";

- absolute limits on permissible concentrations of mercury and cadmium in solid fractions of waste materials; and
- potential disincentives to deep ocean (i.e., off the continental shelf) disposal.

1. Conclusions

The technical environmental conclusions of the initial assessment were as follows:

Overall

- There is an overriding need for a case-by-case approach to the analysis of the environmental feasibility of at-sea disposal of specific FGC wastes. The emphasis in such analyses should be twofold, focusing both on the type of waste and the disposal site environmental conditions.
- All four of the control options considered appeared to be technically feasible. These were:
  (1) dispersed dumping on the continental shelf;
  (2) conventional dumping in the deep ocean (off the continental shelf);
  (3) dispersed dumping off the continental shelf; and
  (4) concentrated dumping of treated (stabilized) wastes on the continental shelf.

The economic feasibility of these control options was regarded as less clear-cut and would serve to limit the viability of several of the technically more promising options.

Specific

- Unless further work contradicts anticipated sedimentation and suspension impacts, the disposal of untreated or treated FGC wastes with soil-like physical properties by bottom-dump barge or outfall on the continental shelf appears to be environmentally undesirable.
- Based on available information on sulfite toxicity, it appeared that an almost immediate (on the order of minutes) dilution factor of greater than 10,000:1 for sulfite alone would be required in the dispersed disposal of untreated wastes containing large fractions of sulfite. The technology was not available for attaining such dilution factors in an economical manner.

Therefore, the dispersed disposal of soil-like, sulfite-rich wastes either on or off the continental shelf was not considered a promising option at that time. It was felt that further information on organism responses to oxidizable sulfur could justify reevaluation of this conclusion.

- Several disposal options appeared promising and were recommended for further research. These included:
  - dispersed disposal of untreated sulfite-rich FGC wastes on the continental shelf;
  - concentrated disposal of treated brick-like FGC wastes on the continental shelf;
  - dispersed disposal of untreated sulfate-rich FGC wastes in the deep ocean; and
  - concentrated disposal of both untreated sulfate-rich FGC wastes and treated FGC wastes in the deep ocean.

The overall conclusion in the category of regulatory considerations was that, given the apparent vigilance in agency attitudes towards ocean dumping, the existing regulations appeared adequate to ensure protection of the ocean environment. However, the following specific comments were considered appropriate:

- There were pending revisions to the then-existing ocean dumping regulations that would allow additional empirical considerations (e.g., field data and models) in the determination of limiting permissible concentrations in the ocean at the disposal site.

- Consideration of the actual anticipated long-term availability of mercury and cadmium in solid fractions of wastes, on a case-by-case basis, could give a better measure of expected environmental effects; and

- Any disincentives to deep ocean dumping should be continually evaluated in light of the apparent desirability of certain deep ocean disposal options.

2. Recommendations for Additional Research

The research needs considered most important based upon the initial assessment were the following:

- A body of empirical data needed to be developed concerning the physical fate and dissolution rates of various types of FGC wastes under conditions that would be representative of ocean disposal area environs.

- Empirical values for uptake of both liquid and solid constituents of FGC wastes by various marine organisms needed to be developed. In particular, values for uptake associated with short-term exposure of pelagic organisms were judged to require investigation.

- Lethal and sublethal effects thresholds needed to be developed for a variety of representative marine organisms upon exposure to FGC wastes. One of the focal points of such research should be the dynamics of food web transfer of potential toxicants contained as trace contaminants in some FGC wastes.

- Mechanisms for eliminating then-extant economic disincentives to deep ocean disposal needed to be developed.

C. REFINED ASSESSMENT

In light of the issues and research needs identified in the initial assessment, the second phase of work under this program, the "refined assessment" (2), focused on physical and chemical investigations with FGC wastes in seawater. Laboratory testing and related assessment efforts involved three subject areas:

- physical fate of untreated FGC wastes in the water column;

- physical fate of untreated FGC wastes on the ocean bottom; and

- chemical fate of untreated FGC wastes in seawater.

1. Conclusions

Upon completion of the refined assessment, the two overall conclusions of the initial assessment were still considered valid. These emphasized the need for case-by-case analyses of prospective at-sea disposal of FGC wastes and affirmed the technical feasibility of available control options. Other specific initial conclusions were modified and/or reinforced in the refined assessment and were summarized as follows (2):

- Unless further work contradicts observed and anticipated benthic sedimentation impacts including mudflows, the disposal of unstabilized FGC wastes with soil-like physical properties by bottom-dump barge or outfall on the continental shelf appears to be environmentally undesirable .

- The problems of disposal of sulfite-rich FGC wastes, both on and off the continental shelf, appeared to be much greater than the problems associated with other FGC wastes. There appeared to be special grounds for concern over the potential for oxygen depletion in the vicinity of masses of sulfite-rich waste. Sulfite toxicity itself may be a relatively minor (secondary) problem because of the significant rate of oxidation depletion.

- Disposal options which still appeared promising and were recommended for further research include:

  - dispersed disposal of untreated sulfate-rich FGC wastes on the continental shelf;

  - concentrated disposal of treated brick-like FGC waste on the continental shelf;

  - dispersed disposal of treated brick-like FGC waste on the continental shelf;

  - dispersed disposal of unstabilized sulfate-rich FGC wastes in the deep ocean; and

  - concentrated disposal of both stabilized and unstabilized sulfate-rich FGC wastes in the deep ocean.

The overall conclusion of the regulatory portion of the assessment was that if there was vigilance in agency attitudes towards ocean dumping, the regulations as revised in 1977 appeared generally adequate to ensure protection of the ocean environment. Specific comments considered appropriate were as follows:

- It appeared that a situation could arise where the absence of adequate baseline data on a potential FGC waste disposal site (a federal responsibility) could lead to inaction or denial of a permit application. If so, this could act as a deterrent to the choice of a new dump site or unreasonable constraint on a permit action when these actions would be environmentally superior to alternative means of disposal.

- There is a criterion of disposal site background plus 50% for incremental additions of mercury and cadmium to area sediments. This criterion appeared to allow the possible incremental addition of cumulative FGC waste-related toxicants at locations where undesirably high ambient concentrations already exist.

2. Recommendations for Additional Research

The following research needs were believed most important based upon the refined assessment:

- empirical bioassay data on the acute and chronic effects of sulfite-rich and stabilized FGC wastes on representative marine organisms;
- empirical bioassay data on the long-term availability and accumulation of FGC waste-related metallic trace contaminants;
- empirical bioassay data on the suitability of soil-like and stabilized FGC materials as benthic substrates in quiescent waters;
- empirical data and verified models to predict field-scale FGC waste behavior during descent through marine water columns; and
- continual investigations of the few field situations where FGC wastes have entered or been placed in marine environments.

D. PURPOSE, SCOPE, AND APPROACH OF ACTIVITIES REPORTED IN PART ONE

The purpose of this phase of the program was to fulfill several of the research needs identified in both the initial and refined assessments. These needs consisted of developing basic bioassay data on the effects of untreated FGC wastes on representative marine organisms. Specific experiments were designed to provide information on the following subject areas:

(1) acute toxicity of sulfite-rich and sulfate-rich unstabilized FGC waste to members of the marine water column;

(2) chronic toxicity of sulfite-rich and sulfate-rich unstabilized FGC wastes to members of marine benthic communities;

(3) suitability of unstabilized sulfite-rich and sulfate-rich FGC wastes as substrates for marine benthos;

(4) leaching behavior of metallic trace contaminants in unstabilized FGC wastes in seawater; and

(5) bioaccumulation of FGC waste metallic trace contaminants by marine benthos.

Two series of experiments were designed by staff of Arthur D. Little, Inc. and the New England Aquarium (NEA) to investigate the above subject areas. Details of the experimental designs are presented in the Appendix to this report. All testing was performed at the NEA.

The first series of tests consisted of measurements of the acute toxicity of various unstabilized FGC wastes to marine zooplankton and finfish, with the wastes maintained in suspension in the water column. The second series of tests was conducted in two parts. First, a series of quiescent and agitated leaching tests was performed to determine the amounts of selected metallic trace contaminants that would leach from the test materials under different conditions. Then, 30-day exposure tests were performed in flow-through seawater systems with partial FGC waste substrates and representative benthic marine plants, invertebrates, and finfish. Organisms from these tanks and from control tanks with sand substates were sacrificed at intervals during the experiment for measurement of metallic trace contaminant residues. This series of tests provided an opportunity to observe aspects of chronic toxicity, substrate suitability, and trace contaminant accumulation upon longer-term exposure of marine organisms to various unstabilized FGC wastes.

Identification of waste samples used in the testing is provided in Table 2.

TABLE 2

FGC WASTE SAMPLES USED IN LABORATORY TESTING

Process Source	Sample Code	Waste Type	Waste Form	Acute Toxicity	Thirty-Day Exposure
Dual Alkali	DA1	Sulfite-Rich (without ash)	Filter Cake	---	✓
Direct Lime	L1	Sulfite-Rich (with ash)	Filter Cake	---	✓
Direct Lime	L2	Sulfite-Rich (without ash)	Filter Cake	✓	---
Direct Limestone	LS2	Sulfite-Rich (without ash)	Thickener Underflow[a]	✓	---
Direct Limestone (forced oxidation)	LS3	Sulfate-Rich (with ash)	Filter Cake	---	✓
Acid Scrubbing	G1	Sulfate-Rich (without ash)	Centrifuge Cake	✓	---

---

[a] Settled

Source: Arthur D. Little, Inc.

III. BIOLOGICAL TESTING

A. ACUTE TOXICITY STUDIES WITH UNSTABILIZED FGC WASTES

1. Experimental Design

a. Overall Rationale and Objectives

The results of the initial and refined assessments suggested that suspended FGC waste in the water column following a dump could have several types of adverse impacts on free-swimming biota. First, there was the likelihood that waste particles, like other suspended sediments, could interfere with the respiratory and/or feeding activities of biota. Second, there was the potential that certain FGC wastes would be unusually toxic due to the potential for sulfite-related oxygen depletion or direct sulfite toxicity. To test these possibilities, a series of experiments was designed to establish the concentrations of sulfite-rich and sulfate-rich FGC wastes that would be lethal to 50% of the test organisms upon 96 hours of exposure.

b. Selection of Test Materials

Because the objective of this experiment was to identify the basic toxic properties of FGC wastes, waste samples free of fly ash were chosen for the test work. This was to avoid potential effects due to the metallic trace contaminants known to be associated with the fly ash fractions of FGC wastes. Two sulfite-rich wastes were chosen, one from a direct limestone scrubbing system (LS2) and one from a direct lime scrubbing system (L2) along with one sulfate-rich (gypsum) waste (G1). Both the sulfite-rich wastes had a sulfite-to-sulfate ratio of greater than 2:1. Major chemical constituents of these waste samples are given in Table 3.

c. Selection of Test Species

Consistent with the intent of EPA's Ocean Dumping Regulations, the criteria of expected sensitivity and "representativeness" were important in selecting species for these experiments. The availability of test data on species' responses to other types of suspended sediments for comparison purposes was also considered. Two types of free-swimming organisms were chosen based on these critiera: the finfish *Menidia menidia* (Atlantic silverside) and the zooplankton *Acartia tonsa*. Both of these species had demonstrated sensitivity to various types of suspended sediments in tests reported by Sherk, *et al*. (3). Although both are more common to estuarine than offshore waters, they were considered sufficiently representative of other dump site biota to be used for these tests.

d. Test Conditions

The experimental equipment and procedures are described fully in the Appendix. For finfish testing, 80-liter flow-through tanks were used for the 96-hour test period, with flow rates of five tank turnovers per

TABLE 3

MAJOR CONSTITUENTS OF FGC WASTE SAMPLES USED IN ACUTE TOXICITY TESTING

Sample Designation	Process Source	Waste Form	Waste Type	Wt % Solids[a]	Chemical Analysis (m/moles/g)						Wt % Acid Insolubles
					Ca	Mg	Na	TOS[b]	SO_4	Cl	
L2	Direct Lime	Filter Cake	Sulfite-Rich	52	7.22	0.07	0.03	5.76	1.37	0.03	1
LS2	Direct Limestone	Thickener Underflow	Sulfite-Rich	59[d]	7.06	0.07	0.03	5.24	0.99	0.05	6
G1	Acid Scrubbing	Centrifuge Cake	Sulfate-Rich	83	6.05	0.01	0.02	0.00	6.04	<0.01	<1

---

[a] As-received

[b] Total Oxidizable Sulfur ($HSO_3^- + SO_3^=$)

[c] Insoluble in 1.0 N HCl

[d] Settled

Source: Arthur D. Little, Inc.

day. After several methods were tried, a static zooplankton test medium was developed consisting of periodically inverted 1-liter bottles. This corresponds to the setup used by Sherk, et al. for the same species (3).

Several of the modifications to the experimental procedures that occurred during the execution of the tests are considered important enough to mention here. As the finfish tests proceeded, the importance of sulfite-related oxygen depletion became readily apparent. To test the sensitivity of the experiment to the reaeration that occurred in the 80-liter tanks (but might not occur in an ocean water column), nitrogen purge was used in some of the later tests with the sulfite-rich FGD wastes (L2 and LS2). In the finfish tests with the sulfate-rich (gypsum) waste (G1) it became necessary to increase pumping rates in order to suspend large amounts of the material. This resulted in 15% mortality in the control tank, which was considered marginally acceptable for continuation of the experiment.

The zooplankton test systems also experienced high control mortalities until a feeding protocol was established. It was recognized that such a protocol was not part of the EPA's recommended bioassay procedures for the ocean disposal program. However, after discussions with staff of EPA's Environmental Research Laboratory (ERL) at Narragansett, Rhode Island, it was concluded that feeding was both acceptable and realistic in light of the experimental objectives.

2. Results and Discussions

The full results of the acute toxicity tests are presented in the Appendix. Summaries of the major findings are presented below.

a. Finfish Tests with Sulfite-Rich FGD Wastes

Preliminary range-finding tests were begun by exposing Atlantic silversides to the sulfite-rich FGD waste from a direct limestone scrubbing system (LS2) at doses corresponding to concentrations of 300, 400, and 500 ppm. All these concentrations produced immediate, dramatic results in the form of oxygen depletion and complete mortality of test organisms in a few minutes of exposure. The same results were obtained with the same concentrations of the sulfite-rich lime system waste (L2). Further testing was conducted with the sulfite-rich lime system waste at concentrations of 100, 200, and 300 ppm, using a nitrogen purge to prevent surface reaeration. The results are shown in Table 4. As in the earlier tests, the concentration of 300 ppm produced significant DO depletion and 90% mortality within ten minutes of the time of initial exposure. However, the 100 and 200 ppm additions as well as the control system each exhibited only 10% mortality upon conclusion of the 96-hour exposure period. These results strongly suggest the following:

(1) that the mechanism of oxygen depletion dominates any other potential mechanism of direct, acute toxicity for sulfite-rich wastes under well mixed conditions; and

TABLE 4

96-HOUR BIOASSAY RESULTS

Experiment Number: 5
Waste Type: L2
Test Started: 16:45 A.M.
Date: July 18, 1977

Species: *Menidia menidia*
Waste Concentration: A. 100 ppm
B. 200 ppm
C. 300 ppm

No. of Organisms: 20/test
20/control

	Makeup Addition Time	T, °C	Sal., %	Dissolved Oxygen, mg/ℓ				NH_3 µgN/ℓ	TSS mg/ℓ	$SO_3^=$ x 10^6 m/ℓ Slurry	$SO_3^=$ x 10^6 m/ℓ Aqueous	Ca Slurry	Ca Aqueous	Cumul. No. Dead Animals
Sampling Time				0.1						0.1	0.1			0.1
Control		21.5	31.0	7.1						0	0			0
A		21.0	31.0	6.0						3476	3476			0
0-hr B		21.0	31.0	4.7						4009	3676			0
C		21.0	31.0	3.5						9546	7678			18
Sampling Time		23.7	23.7	23.7				17.3		23.9				
Control		22.0	31.0	7.2				154		0	N.D.			0
A	18.7	23.0	30.5	6.2				154		497				1
24-hr B		23.0	31.5	4.8				182		506				0
C		23.0	31.0	5.9				210		561				18
Sampling Time		45.0	45.0	45.0						44.6				
Control		21.5	31.5	7.0						0	N.D.			1
A	43.5	22.0	31.0	6.0						676				2
48-hr B		22.0	31.5	5.7						488				1
C		22.0	31.0	6.4						518				18
Sampling Time		69.0	69.0	69.0						68.8				
Control	65.2	22.0	31.5	7.1						0	N.D.			2
A		22.5	31.0	5.0						0				2
72-hr B		22.5	31.5	4.3						56				2
C		22.5	31.5	5.8						102				18
Sampling Time		90.1	90.1	90.1				90.2		89.8				
Control	89.3	22.5	32.5	7.1				224		0	N.D.			2
A		23.0	32.0	5.5				182		203				2
96-hr B		23.0	32.0	4.8				238		249				2
C		23.0	32.0	5.9				252		425				18

Source: New England Aquarium

(2) that the sulfite-rich waste concentrations between 200-300 ppm represent a lower limit associated with rapid oxygen depletion and high finfish mortality under well mixed conditions.

The results of modelling efforts based on laboratory-scale "drop tests" earlier in this program indicated that it is not unreasonable to expect concentrations in excess of 200 ppm in the immediate vicinity of a descending FGD waste mass from a conventional ocean dump (2). However, this expectation has not been confirmed by field-scale experimental observations. Neither has it been demonstrated that finfish will avoid or be attracted to descending masses of FGD waste. It is believed that the experimental conditions in the last of the NEA tests described above represent "worst case" circumstances not likely to be achieved in an actual disposal situation where less complete mixing would occur. In spite of these caveats, the results of these tests do provide a basis for serious concern over the potential acute toxicity of conventionally dumped sulfite-rich FGC wastes in the ocean.

b. Finfish Tests with Sulfate-Rich FGD Waste

The test protocol followed for the two sulfite-rich waste was repeated for a sulfate-rich (gypsum) waste. When equipment was finally available to suspend sufficient quantities of the sulfate-rich waste, preliminary range-finding tests indicated that the 96-hour LC_{50} appeared to fall somewhere between 5,000 and 10,000 ppm. Definitive tests indicated an LC_{50} value of about 2,000-2,500 ppm. These results can be compared to the results reported by Sherk, *et al*. (3) for exposure of the same species to other types of suspended sediments. These authors reported a 24-hour LC_{10} value of 570 mg/ℓ and a 24-hour LC_{50} of 2,400 mg/ℓ for Atlantic silversides exposed to suspensions of Fuller's Earth. The silversides was among the most sensitive species tested (3).

The following conclusions can be drawn from these results:

(1) There is a strong reason to believe that the ocean dumping of "clean" sulfate-rich FGD wastes (i.e., those free of fly ash) represents no more of a threat to marine pelagic finfish in the water column than does the disposal of other "clean" sediments such as certain dredged materials; and

(2) There is no apparent reason to believe that this impact potential by itself would be sufficient to limit the conventional dumping of this particular type of FGD waste at any approved dump site.

c. Zooplankton Tests with Sulfite-Rich FGD Waste

The acute toxicity of the sulfite-rich FGD waste from the lime scrubbing process (L2) was determined in 48-hour tests for the zooplankton *Acartia tonsa* after completion of the aforementioned 96-hour tests with the same waste and the finfish *Menidia*. After 48 hours of exposure the control, 25 ppm, 50 ppm, and 100 ppm waste exposure tanks showed, respectively, 10%, 3%, 22%, and 10% mortality. At a waste exposure concentration of 150 ppm all the test animals died within 24 hours. The 48-hour LC_{50} appeared to be between 100-150 ppm. Again, sulfite-related oxygen depletion appeared to be responsible for the observed mortality, with DO levels dropping to 2.7 ppm after 48 hours in the 100 ppm waste exposure, and 0.8 after 24 hours in the 150 ppm waste exposure. Thus, the conclusions stated above regarding the potential acute toxicity of conventionally-dumped, unstabilized sulfite-rich FGC wastes to finfish also apply to zooplankton, with the further suggestion that waste concentrations lower than 200 ppm (i.e., on the order of 100-150 ppm) could be problematic. From the standpoint of potential field-scale impacts, it is considered unlikely that zooplankton could (or would) actively avoid or approach descending masses of sulfite-rich waste. It is considered likely that only those in the descent path would be effected and that the loss of this number of zooplankton would not have a measurable adverse impact on the pelagic community at a dump site. This is because the zooplankton of the ocean are very abundant, have patchy distribution, and have short life cycles and population recovery times.

d. Zooplankton Tests with Sulfate-Rich FGD Waste

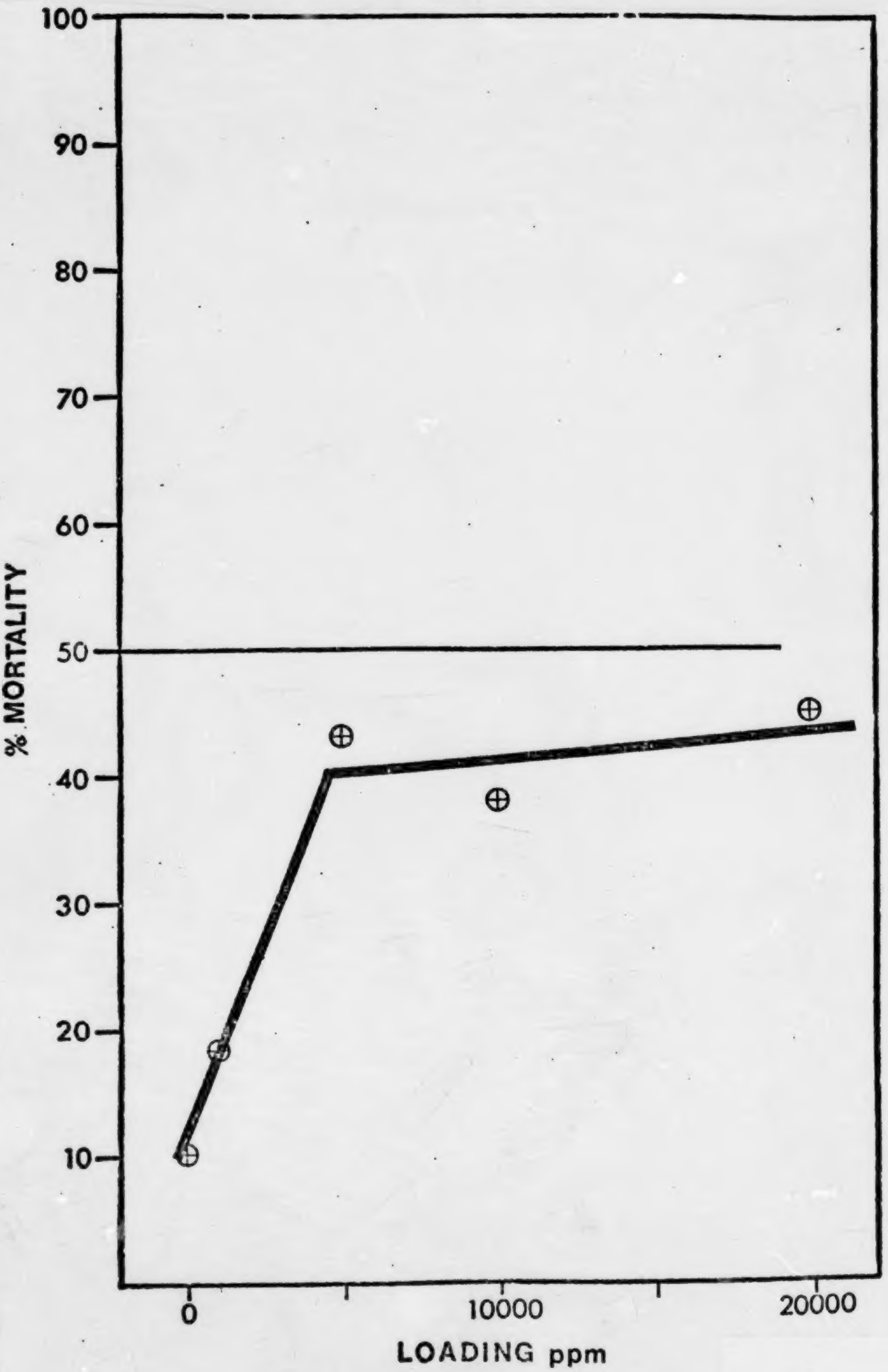
The gypsum waste used for the aforementioned finfish tests was used for 48-hour acute toxicity tests with the zooplankton *Acartia tonsa*, following the same protocol as for the tests with the sulfite-rich material and this species. After 48 hours of exposure including regular, periodic suspensions of the waste material, the control 1,000 ppm, 5,000 ppm, 10,000 ppm, and 20,000 ppm containers showed, respectively, 10%, 18%, 44%, 38%, and 45% mortality (see Figure 1). Although these results do not actually define an LC_{50}, they strongly suggest the nature of the threshold concentrations associated with adverse effects and may be compared with the results of Sherk, *et al*. (3). These investigations reported that *Acartia tonsa* exhibited reductions in feeding efficiency (measured as carbon uptake) of 20-100% when exposed for short (5-10 minutes) and somewhat longer (125 minutes) periods to suspended sediment concentrations of 50-10,000 mg/ℓ. It is not unreasonable to associate a similar cause-effect relationship with the increased mortalities observed in this part of the NEA test program.

The two conclusions stated above for the finfish tests with the ash-free, sulfate-rich (gypsum) FGD waste also apply to the zooplankton test results. Further, the potential for adverse impacts of this type of FGD material on zooplankton at a dump site is rendered negligible by the distribution, abundance, and population dynamics of zooplankton in the ocean (see Section III.A.2.c. above).

FIGURE 1

48-HOUR BIOASSAY

Waste G-1 - *Acartia tonsa*



Source: New England Aquarium

B. THIRTY-DAY EXPOSURE STUDIES WITH UNSTABILIZED FGC WASTES

1. Experimental Design

a. Overall Rationale and Objectives

The initial and refined assessments in this program identified two potential impact issues that would result from the long-term presence of FGC wastes on the ocean floor at a dump site. These issues were: (1) physical suitability of the fine-grained wastes as substrate for use by marine benthos; and (2) chronic toxicity of the waste substrate, especially due to the potential availability of metallic trace contaminants. The results of the acute toxicity studies discussed in Section IILA above provided the basis for an additional concern, i.e., that periodic resuspension of accumulations of sulfite-rich waste materials on the ocean floor could lead to instances of organism mortality due to depletion of dissolved oxygen. The chronic exposure studies discussed below were designed in an effort to provide basic empirical data regarding the potential for each of these types of impacts.

Because of the emphasis on trace contaminant impacts in these studies and the knowledge that fly ash is a reservoir for many FGC trace contaminants, two of the three wastes selected for testing were FGD wastes containing fly ash which had been simultaneously collected or admixed. One was a sulfite-rich material from a lime scrubbing system (L1); the second was a sulfate-rich waste from a limestone system (LS3). The third waste used in this series of tests was a sulfite-rich FGD waste from a dual alkali scrubbing system containing no fly ash (DA1). This choice of wastes created the opportunity to test independently the potentials for chronic sulfite-related toxicity and trace element contamination. Composition of these wastes is given in Table 5.

b. Physical/Chemical Considerations - Preliminary Tests

In order to design an experimental procedure that would simulate the environment to which organisms may be subjected after FGD waste materials had been disposed of in the ocean, an understanding of the chemical behavior of the waste in the ocean environment was required. The need for this understanding was further accentuated by the fact that it is not possible to simulate the expected type of actual exposure in a laboratory test where a sample of the waste is simply placed in an aquarium containing the organism in flowing seawater. The required turnover and filtering would severely reduce the trace element levels that may be produced due to leaching from the waste. However, without filtration or replenishing of seawater, the excretion of wastes by the test organisms would cause the ammonia level in the water to rise to toxic levels.

In order to overcome these difficulties, it was necessary to use a continuous flow system with inflowing fresh seawater which contained trace elements at similar concentrations to those that would be produced by leaching from the waste. This configuration allowed for a nontoxic

TABLE 5

MAJOR AND TRACE COMPOSITION OF WASTE SAMPLES TESTED

Component	Sample DA1	 L1	 LS3
Major:			
% Solids	54	63	79.3
Ca^{2+} (mmoles/g dry)	7.15	4.59	4.20
TOS[a]	5.52	3.85	0.01
$SO_4^=$	0.97	0.70	3.69
Na^+	0.43	0.03	0.03
Mg^{2+}	0.25	0.045	0.04
Cl^-	0.037	0.052	0.05
Acid Insolubles (5)	0.00	35.2	37.6
Alkalinity (mm OH^-/g dry)	0.59	NA	NA
Trace (ppm dry)[b]:			
Zn	(c)	59 ± 10	91 ± 6
Cd	0.29 ± 0.06	0.8 ± 0.2	1.1 ± 0.2
Ni	11 ± 2	44 ± 10	18 ± 3
Hg	0.56 ± 0.04	0.17 ± 0.02	0.28 ± 0.01
Se	15 ± 1	19 ± 2	25 ± 2

NA - Not analyzed but much lower than DA1. See reference (4).

[a] Total oxidizable sulfur.

[b] Average of 2-6 measurements using nitric/sulfuric acid dissolution.

[c] Data obtained showed highly variable results between 0.3-275 ppm.

Source: Arthur D. Little, Inc. and New England Aquarium

ammonia level and for continuous exposure to the trace element levels which might be experienced in the environment. A much lower trace element level would have occurred in some of the tests if the influent water were not supplemented with some of the elements. In order to choose proper trace element levels for exposure, it was necessary to conduct two experiments which would yield data on the level of trace elements that might occur after an ocean dump. One experiment was a leaching of the wastes by seawater under stirred or well mixed conditions. This provided data on "worst case" release of the trace elements into the overlying seawater. The other experiment was a leaching of the wastes under quiescent conditions, which more closely simulated the environment on the ocean bottom in the absence of any bottom currents. Using these results, realistic "conservative" conditions for the selected trace elements were chosen and maintained in the continuous flow exposure experiment.

(1) Design of Quiescent Leaching Test

This experiment was designed to determine the quantity of selected trace elements (Zn, Cd, Ni, Se) that would be released into seawater from the FGC waste disposed on the ocean bottom and in contact with relatively quiescent seawater. These elements were selected on the basis of impact priorities identified in previous phases of the program and after preliminary tests showed that a fifth, high priority, element, Hg, could not be detected in leachate above the levels in background Boston Harbor water. It would be expected that under these conditions the rate of trace element release would be governed mainly by the rate of release from individual waste particles and the diffusion rate of the elements through the interstitial liquid. The trace elements present in the uppermost layer of the disposed waste, which directly contacts the seawater, are expected to be more available to the seawater than those from subsequent underlying layers which required dissolution and diffusion to reach the seawater. If mixing of waste and seawater occurred on the ocean bottom during ocean bottom "storms," then the effect of liquid phase diffusion on trace element levels would be less important on a relative basis.

Thus, based upon the above discussion, the physical parameters which may play an important role in determining the amount of trace elements released include the surface area of the waste, depth of the disposed waste, and time of contact of the waste and overlying seawater. The chemical factors of principal importance are waste composition. The composition of the seawater and temperature of extraction also play an important role in the rates and amounts released, but they do not vary to a great enough extent to make them a variable and were assumed and held constant.

The test parameters used took into consideration the following criteria. The length of the test (31 days) was chosen based on the assumption that major wave-induced mixing events (and therefore dilution) would occur on the continental shelf ocean floor on the average of about once every two to four weeks. Thus, maximum trace element buildup would occur just prior to the mixing. Also, since diffusion in the liquid phase is slow (in the absence of mixing, coefficients of $\sim 10^{-5}$ cm^2/second are observed), only the top

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

10-15 cm of the waste layer would play an important role in this time period and, thus, waste heights of a few centimeters were used. (For comparison, a waste height of about 100 cm may be expected in a shallow disposal area from a barge filled with 300 m^3 of waste). Using this reasoning, a disposal pile which is 100 cm high may produce a similar amount of trace elements to one which is 300 cm high for a similar contact time with the ocean water. However, by increasing the surface area of the pile, an increase in trace element release may be expected proportional to the surface area. The ratio of seawater to waste would affect the net concentration of trace elements dissolved but not the total amount released for a fixed amount of waste and contact time.

The experimental apparatus used in this test is shown in Figure 2. An 80-liter fiberglass aquarium was used, measuing 53 cm x 38 cm x 36 cm (bottom area of 2,000 cm^2) and equipped with a low rate of agitation (rpm) from a bent glass rod stirrer. The stirrer design and speed was such that it maintained the liquid phase homogeneous but did not suspend any solids. The amount of trace elements released was determined by sampling of the liquid phase. Typically, one liter of sample was taken. The tank bottom was completely covered with the waste sample to various depths. Filtered seawater (0.45 μm) was added on top of the waste carefully to minimize suspension. Three waste samples, sulfite-rich without ash (DA1), sulfite-rich with ash (L1), and sulfate-rich with ash (LS3) were tested. The detailed experimental parameters are summarized in Table 6. Experiments A through C were designed to show variations between the waste under similar conditions. Experiments C through E were designed to test variations in waste depth. A control of seawater was also run during the test to check on possible contamination from external sources.

The tanks containing sulfite-rich wastes were continually purged with nitrogen to prevent oxidation. The tanks were covered with polyethylene to minimize contamination. Samples of the seawater were taken after various times (e.g., 1, 7, 11, 14, and 31 days) of contact and filtered through a 0.45 μm filter. These samples were analyzed for Se, Cd, Ni, and Zn as described in the Appendix.

(2) Design of Stirred Leaching Test

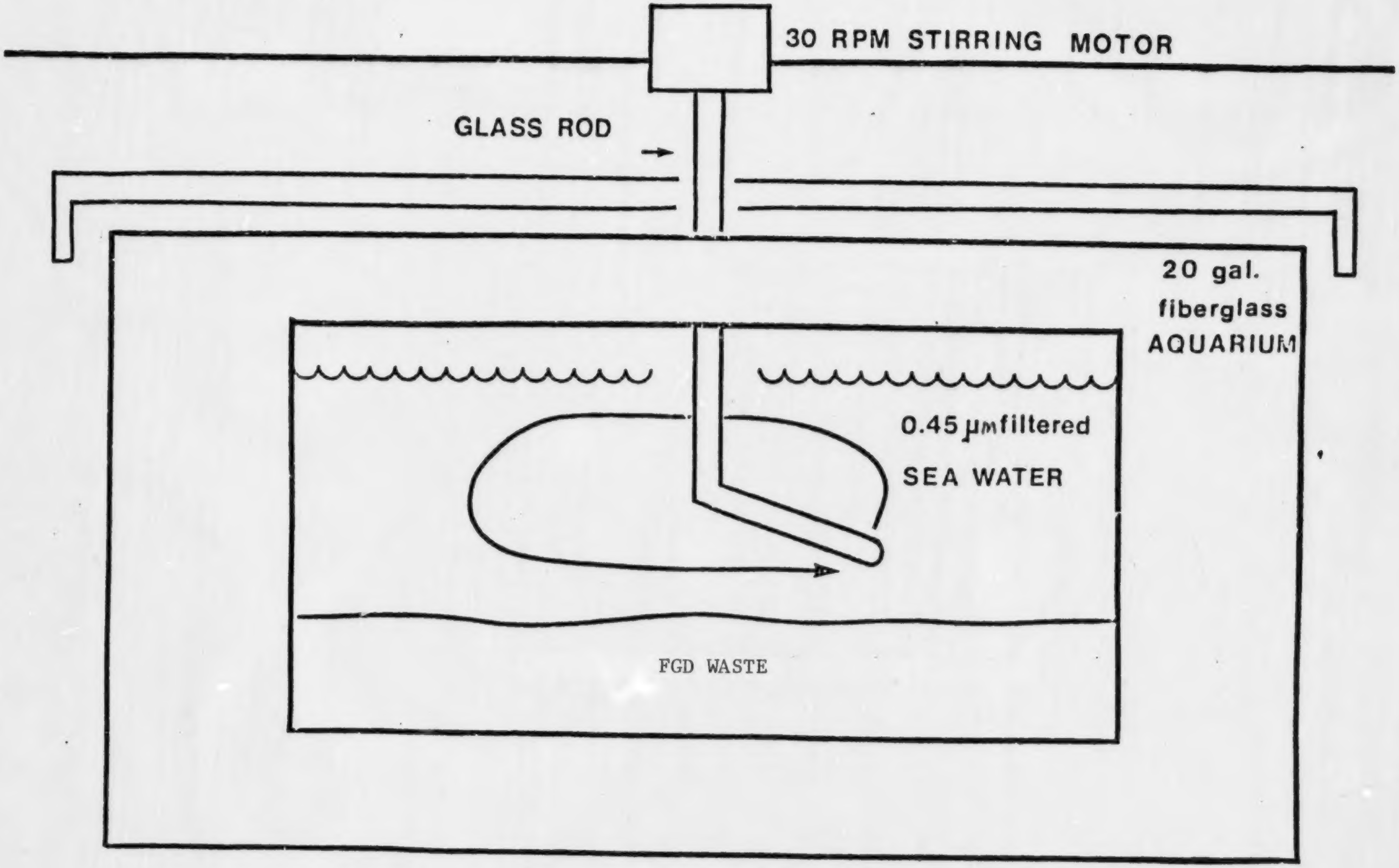
Stirred leaching tests were conducted in order to obtain data on the amount of the selected trace elements that would leach under "worst case" turbulent mixing conditions. These experiments were conducted using a one-liter container equipped with a teflon mechanical stirrer to suspend the particles. Two slurry concentrations were used (∿5% and 25%). Samples were withdrawn after 2, 4, and 7 days and analyzed for the selected trace elements after filtration through 0.45 μm filter (see the Appendix).

In order to assess the extent of leaching of the trace elements from the waste, the total concentration of these elements in the waste were determined. Measurements of Zn, Cd, Ni, Hg, and Se were performed on samples of the waste which were freeze-dried using the procedures given in the Appendix.

For Page Numbering

FIGURE 2

EXPERIMENTAL SETUP FOR QUIESCENT LEACHING TEST


30 RPM STIRRING MOTOR
GLASS ROD
20 gal. fiberglass AQUARIUM
0.45 µm filtered SEA WATER
FGD WASTE

Source: New England Aquarium

TABLE 6

EXPERIMENTAL PARAMETERS USED IN QUIESCENT LEACHING TESTS

Experiment	Tank No.	Material[a]	Waste Height	Amount of Waste[b]	Sea Water Volume
A	1	DA1	6.3 cm	23.4 kg	15.8 L
B	2	L1	6.8 cm	23.4 kg	15.8 L
C	3	LS3	5.8 cm	23.4 kg	15.8 L
D	4	LS3	1.5 cm	6 kg	46 L
E	5	LS3	13 cm	52.4 kg	30 L
Control	6	Seawater	None	None	50 L

---

[a] DA1: Sulfite-rich without ash.
L1: Sulfite-rich with ash.
LS3: Sulfate-rich with ash

[b] Net weight.

Source: Arthur D. Little, Inc. and New England Aquarium

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

c. Design of Thirty-day Biological Exposure Tests

The thirty-day exposure tests were carried out in four large tanks (90 cm x 60 cm x 30 cm) with volumes of 146 liters to the overflow and four smaller tanks (55 cm x 40 cm x 30 cm) with volumes of 60 liters to the overflow. The larger tanks were designed to hold the flounder (*Pseudopleuronectes americanus*) and the smaller for the clams (*Mya arenaria*), snails (*Littorina littorea*), and eelgrass (*Zostera marina*) (all three in one tank). These organisms were chosen for the chronic exposure tests because all were characteristic of marine benthic environments, and they each exhibited different feeding habits and thereby potentially different mechanisms for organism/waste interaction including burrowing and resuspension. Two of the organisms (flounder and soft clams) are harvested and consumed by man, making them appropriate candidates for studies of trace contaminant accumulation. While it is not a resident of offshore dump sites, eelgrass was the only available experimental vegetation to test the suitability of FGD waste as a substrate for vegetative growth.

Filtered seawater was pumped through a constant temperature bath and manifolded to each of the tanks (see Figure 3). Water flow through each tank was controlled using a PVC needle valve. The volume in the tank was kept constant by having the excess draining via an overflow located near the top of the tanks. Where required based on the results of the leaching tests, trace elements were introduced into certain test tanks using a peristaltic metering pump at a point where it mixed with the influent water.

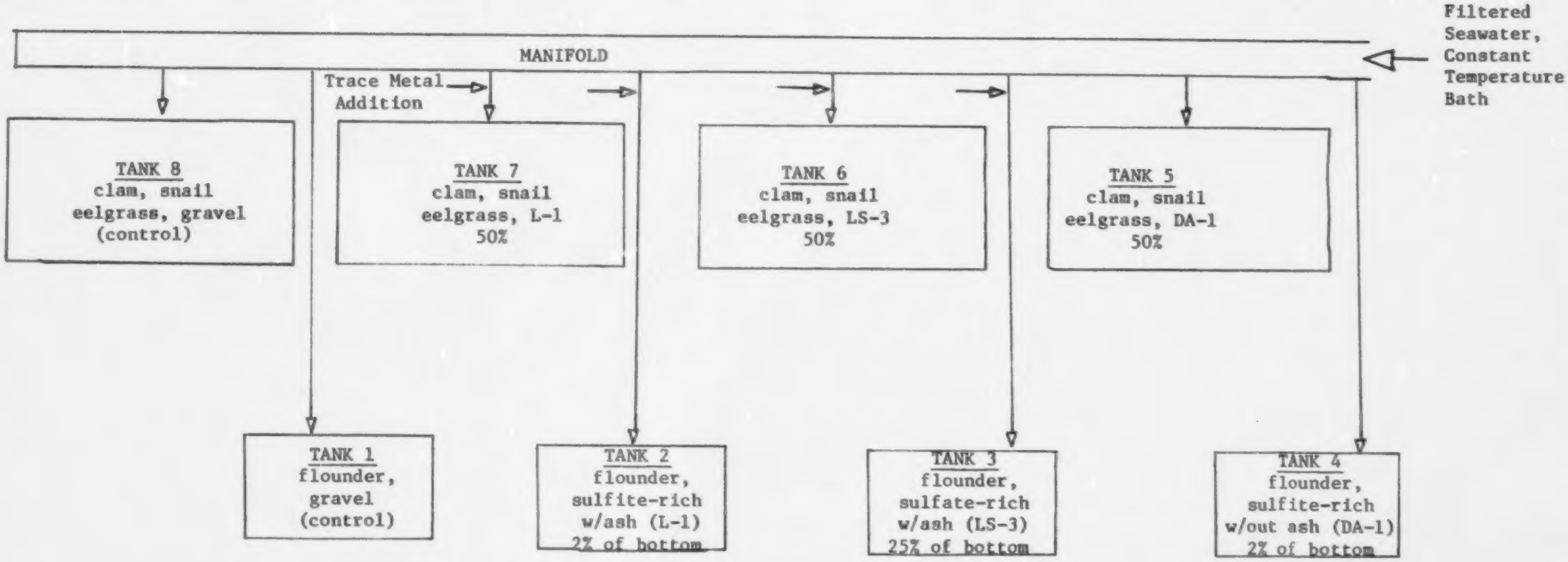
In order to maintain an acceptable ammonia level and consistent flow during the four-week period of the test, flow rates of 0.32 liter per minute (four turnovers per day) and 0.14 liter per minute (five turnovers per day) were used for the larger and smaller tanks, respectively.

Samples of the waste were placed on the bottom of these tanks. The amount of waste placed depended on the tank size, organism, and waste properties. Due to the rapid depletion of dissolved oxygen by the sulfite-rich wastes under turbulent conditions, it was discovered that it was not possible to use a large amount of these materials (DA1 and L1) in the presence of the flounder. The flounder tended to dig into the waste and readily mix it with the seawater. Preliminary tests showed that the flounder could not survive 25% of the bottom being covered with the DA1 waste. However, greater than 90% survival over a three-day preliminary test period was observed for a patch 100 cm^2 (16 sq. inches, or 2% of the bottom surface) in area. Note that this amount, were it agitated, would have been sufficient to kill the fish. In the smaller tanks a large amount of sulfite material did not prove to be a problem with respect to dissolved oxygen depletion, since the organisms placed in these tanks did not stir the waste and water. Greater than 99% survival over a three-day preliminary test period was observed for the clams, eelgrass, and periwinkel where 50% of the bottom was covered with DA1 waste. It was decided not to

For Page Numbering

FIGURE 3

THIRTY-DAY EXPOSURE TANKS SETUP


MANIFOLD
Filtered Seawater, Constant Temperature Bath
Trace Metal Addition
TANK 8
clam, snail
eelgrass, gravel
(control)
TANK 7
clam, snail
eelgrass, L-1
50%
TANK 6
clam, snail
eelgrass, LS-3
50%
TANK 5
clam, snail
eelgrass, DA-1
50%
TANK 1
flounder,
gravel
(control)
TANK 2
flounder,
sulfite-rich
w/ash (L-1)
2% of bottom
TANK 3
flounder,
sulfate-rich
w/ash (LS-3)
25% of bottom
TANK 4
flounder,
sulfite-rich
w/out ash (DA-1)
2% of bottom

Source: Arthur D. Little, Inc. and New England Aquarium

cover the complete area with waste to allow the organisms a choice. The remainder of the bottom was covered with gravel. Larger amounts of the sulfate-rich material (LS3) were used in the flounder tank, since no dissolved oxygen depletion was expected from this waste. One large and one small control tank, each with gravel substrate, was run along with the other tanks. The identity and amount of waste placed in each tank is summarized in Table 7.

The trace element levels to which the organisms were exposed were determined from the results of the quiescent leaching experiments. Since most of the organisms tested tend to reside at the bottom (except for the snails), it is reasonable to assume they would be exposed to high trace element levels due to their proximity to the waste. Thus, a reasonable "conservative" condition was to assume levels as would be obtained if the trace elements leached for 31 days under quiescent conditions into a layer of liquid of four cm above the waste. The resulting levels added to the seawater in some tanks and used as reference points during these studies are given in Table 8. The trace elements were metered from a solution of the metals in seawater adjusted to about pH 6. The zinc, cadmium, and nickel were added as chloride, and selenium as H_2SeO_3. For the larger tanks a stock solution containing these metals at 320 times the final concentration desired was made, whereas for the smaller tanks the levels metered were 140 times the desired concentrations. The metered solutions were added at one mℓ/minute. The range of concentration of these solutions ranged from 1-33 ppm in the metals.

Addition of zinc, cadmium, and nickel as the chloride is reasonable even though the actual speciation of these elements as they leach from the waste is unknown. These elements exist generally only in the +2 oxidation state and are kinetically quite labile. Thus, once they are dissolved in the seawater, they rapidly form the various complex ions which are most thermodynamically stable in the seawater media (e.g., chloro complexes) irrespective of the original form of the addition as long as the addition is not a very stable complex in species. The addition of selenium in the +4 oxidation state (H_2SeO_3, which is the hydrated form of SeO_2) is less certain. However, since selenium probably exists as either Se^o, SeO_2, or SeO_3 and Se^o is not very soluble in water and SeO_3 is a strong oxidizing agent, it is likely that the selenium is present in the +4 oxidation state.

2. Results and Discussion

a. Chemical Composition of the Wastes

The major and some trace element content of the wastes tested were given in Table 5. The DA1 and L1 samples were sulfite-rich, while the LS3 sample had very little sulfite. The ash content (acid insoluble content) of the L1 and LS3 samples ranged between 35-40%. The DA1 sample was highly alkaline compared with the other two samples. For most of the trace metals analyzed the levels in the ash-free sample (DA1) were lower than those in the samples with ash (L1 and LS3). The Se, Hg, and Ni

TABLE 7

LONG-TERM EXPOSURE TESTS - WASTE CONTENT

Tank No.	Organism	Material	Waste Patch Size (cm^2)	% of Bottom Covered with Waste
1	Flounder	Fine gravel (control)	0	0
2	Flounder	Sulfite-rich with ash (L1)	100	2
3	Flounder	Sulfate-rich with ash (LS3)	1350	25
4	Flounder	Sulfite-rich without ash (DA1)	100	2
5	Eelgrass, periwinkle, clam	Sulfite-rich without ash (DA1)	1100	50
6	Eelgrass, periwinkle, clam	Sulfate-rich with ash (LS3)	1100	50
6	Eelgrass, periwinkle, clam	Sulfite-rich with ash (L1)	550	50
8	Eelgrass, periwinkle, clam	Fine gravel control	0	0

Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 8

TRACE ELEMENT CONCENTRATIONS USED IN LONG-TERM TOXICITY TESTS

		Added Concentrations (ppb)[a]			
Tanks	Material	Zinc	Cadmium	Nickel	Selenium
4, 5	DA1	b	b	b	b
2, 7	L1	+3	+4	+20	+106
3, 6	LS3	+25	+18	+18	+95
1, 8	Gravel	b	b	b	b

---

[a] Above background Boston Harbor seawater.

[b] Same as background seawater.

Measured Composition of Boston Harbor seawater:
Zn - 10 ± 0.2 ppb
Se - 7.7 ± 3.2 ppb
Ni - 1.4 ± 0.2 ppb
Cd - 0.8 ± 0.6 ppb

Source: Arthur D. Little, Inc. and New England Aquarium

content of these samples was on the higher end of the range reported for FGD wastes, and the Cd and Zn contents were variable. (4)

b. Stirred Leaching Tests

The amounts of the selected trace elements released from the wastes into seawater after stirring slurries of about 5% and 25% solids for two to seven days are given in Table 9. Plots of the data of μg released versus time are given in Figures 4 through 7. These figures indicate that leaching of most of the elements would continue even after seven days of stirring. The levels of the trace elements were much lower for the DA1 material, presumably due at least in part to the low solubility of these metals in the high pH of the slurry produced. No mercury was detected in any of the extracts. Selenium was extracted in the greatest amount of any trace element analyzed. The percent of trace elements released in comparison to that available in the waste is given in Table 10. Selenium was released to a greater extent than the other metals. In one case, nearly 5% of the selenium was leached in seven days. Similar amounts of cadmium were also leached. Between 1 and 4% of the nickel and zinc leached in seven days.

The concentrations of trace elements compared to the background concentrations observed in Boston Harbor seawater (Table 11) show little difference for the alkaline, ash-free DA1 extracts (except for selenium) and significant differences for the L1 and LS3 extracts. Levels from 3 to 30 times the background levels were observed for most of the metals. The high selenium levels of DA1, as compared with other metals in the extracts, may be explained by the greater pH dependence of the solubility of Zn, Cd, and Ni as compared with Se. DA1 extracts were observed to be highly alkaline (pH 11.2, reference 1) as compared with nearly neutral (pH ∿8) for the other two materials.

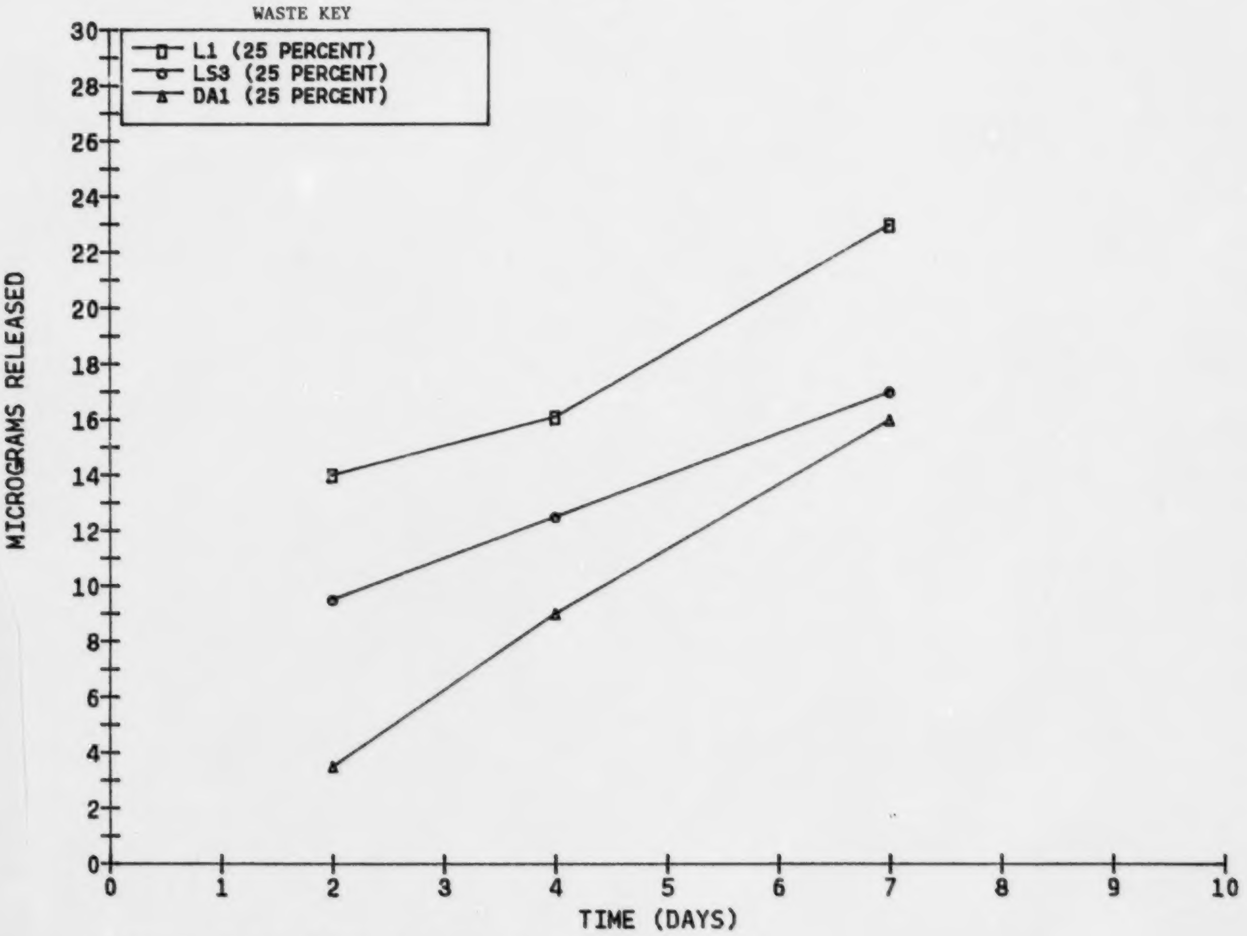
c. Quiescent Leaching Tests

The results obtained for the leaching of the FGD waste materials under quiescent conditions are given in Table 12. The DA1 waste did not show any measurable metals release over the 31-day period. This compares well with the results of the stirred experiment except for the selenium data. Graphs of the amount released versus time for the LS3 and L1 wastes are given in Figures 8 to 12. Figure 8 illustrates that similar amounts of selenium were released from three LS3 tanks with differing waste heights and that release appeared likely to continue beyond 31 days. A similar conclusion may be drawn from the cadmium data for the LS3 tanks (Figure 9). For the L1 material the trace element data are not consistent among the different elements, with the cadmium showing a leveling off; nickel, an increase; and selenium, a decrease with time. The decrease of selenium may be due to readsorption of selenium on the waste.

Comparison of the data from the stirred and quiescent experiments is informative (Table 13). These data indicate that in all cases the μg of element released per 100 g of wet waste was greater for the stirred conditions for similar leaching times. The amount leached was most similar under the stirred and quiescent conditions for Tank 4 (with a

FIGURE 4

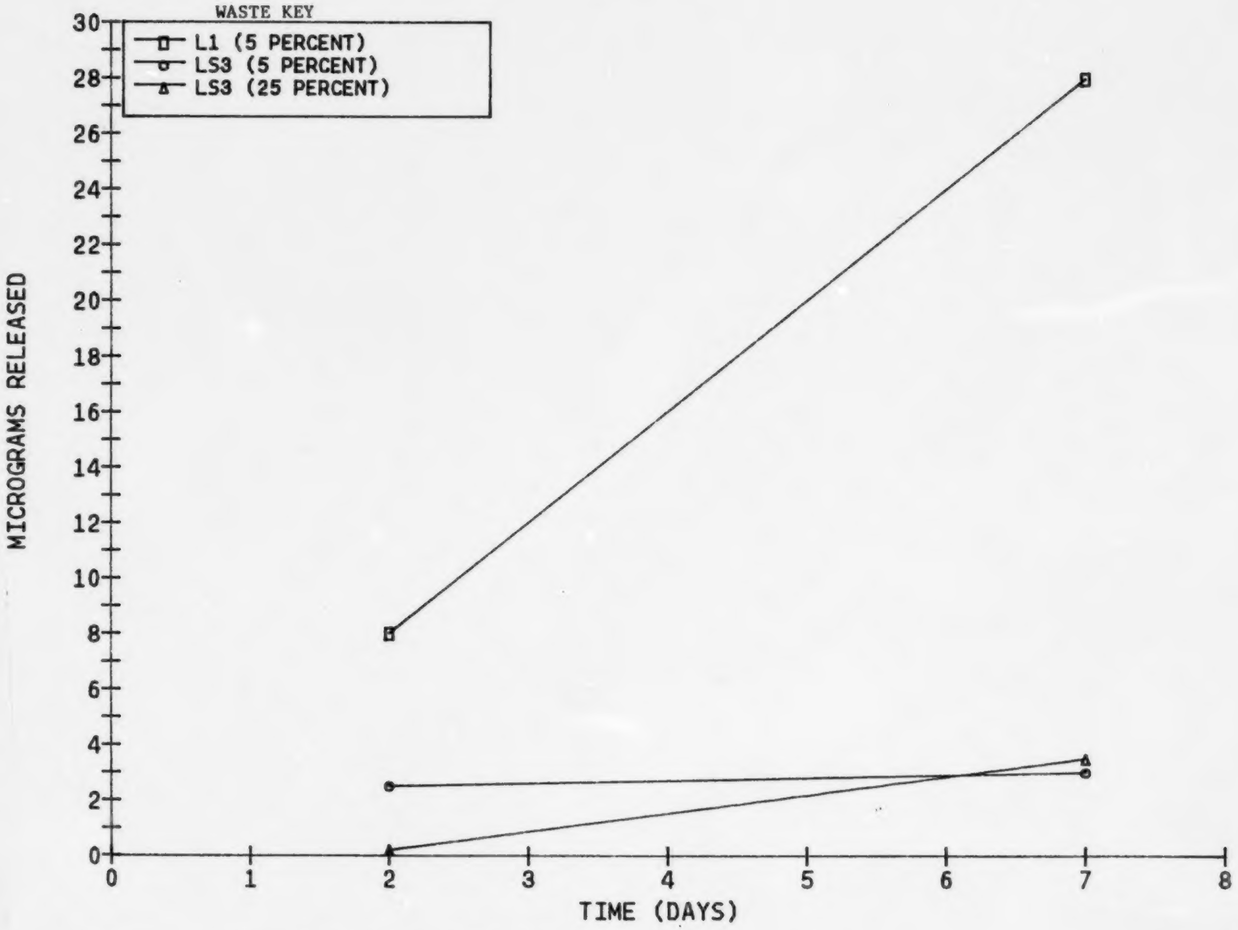
SELENIUM RELEASE (STIRRED EXPERIMENTS)



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 5

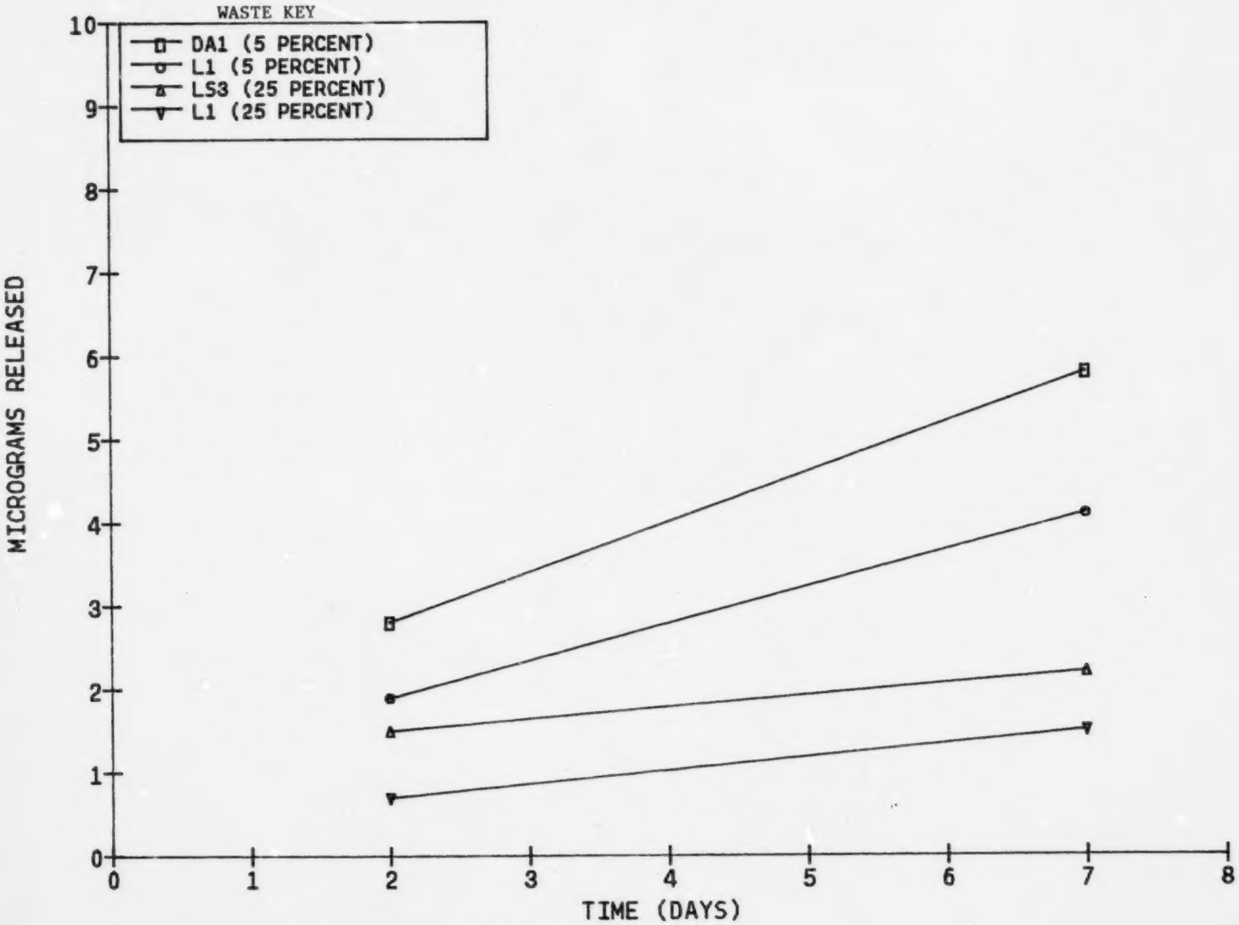
NICKEL RELEASED (STIRRED EXPERIMENTS)



Source; Arthur D. Little, Inc. and New England Aquarium

FIGURE 6

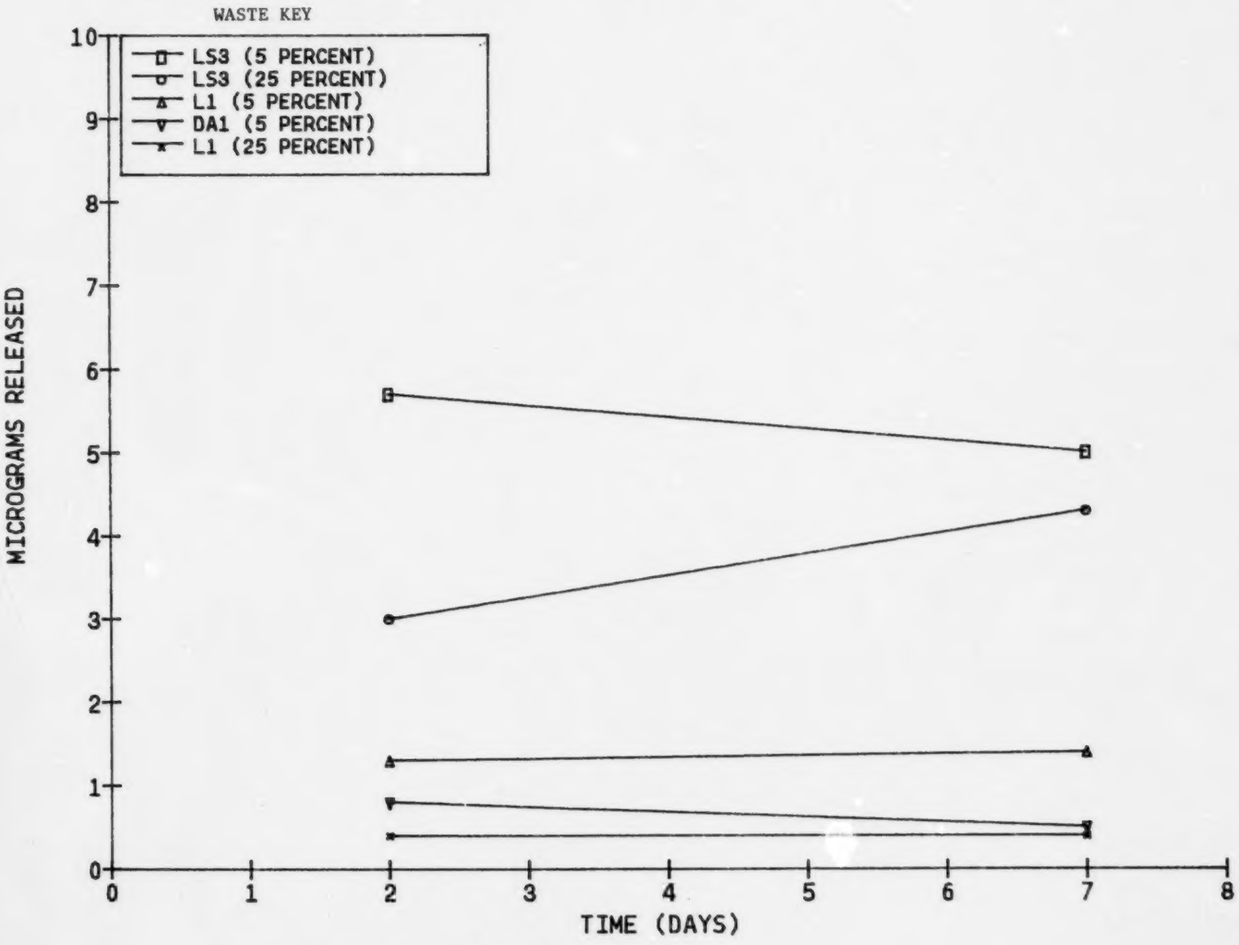
ZINC RELEASED (STIRRED EXPERIMENTS)



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 7

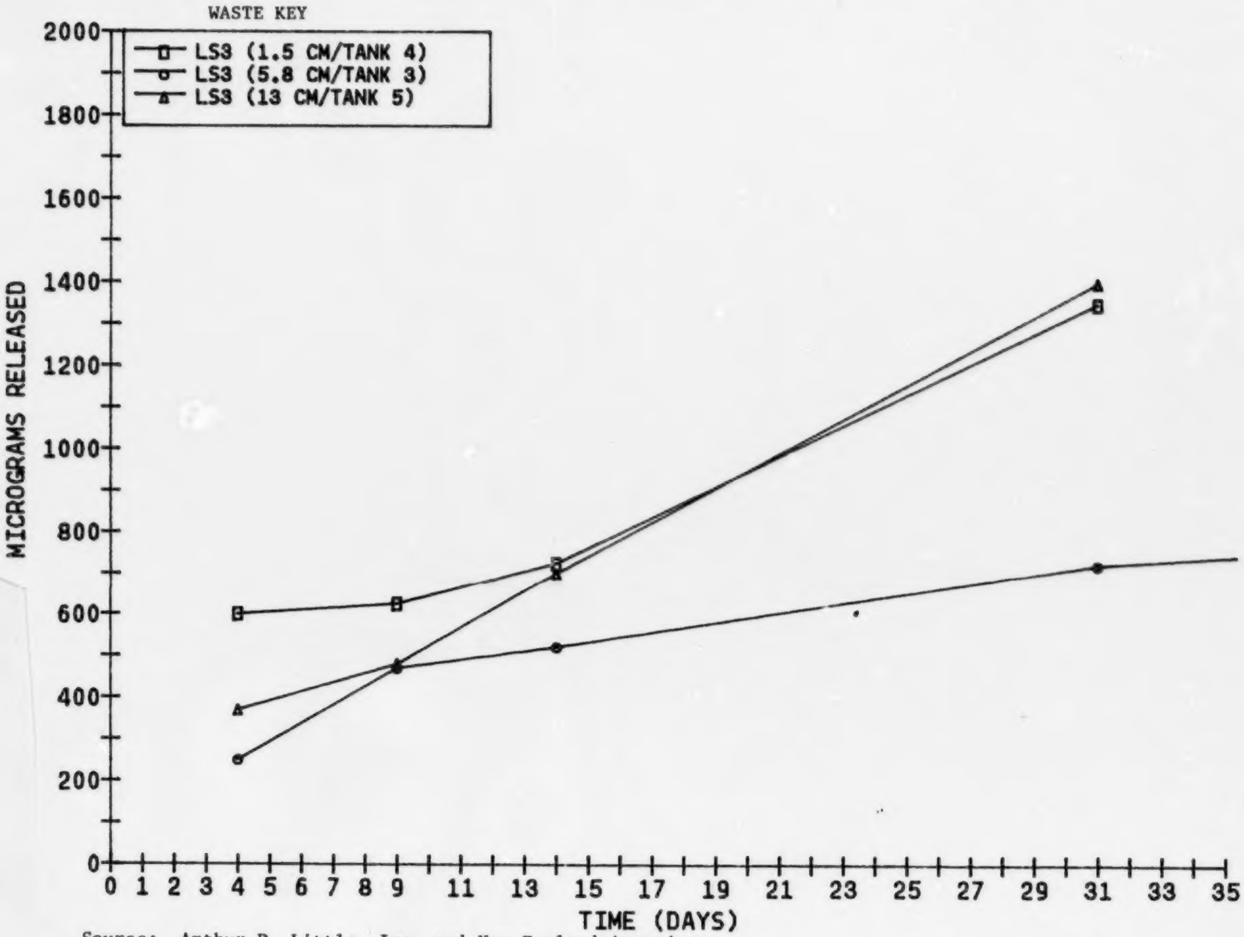
CADMIUM RELEASED (STIRRED EXPERIMENTS)



Source: Arthur D, Little, Inc. and New England Aquarium

FIGURE 8

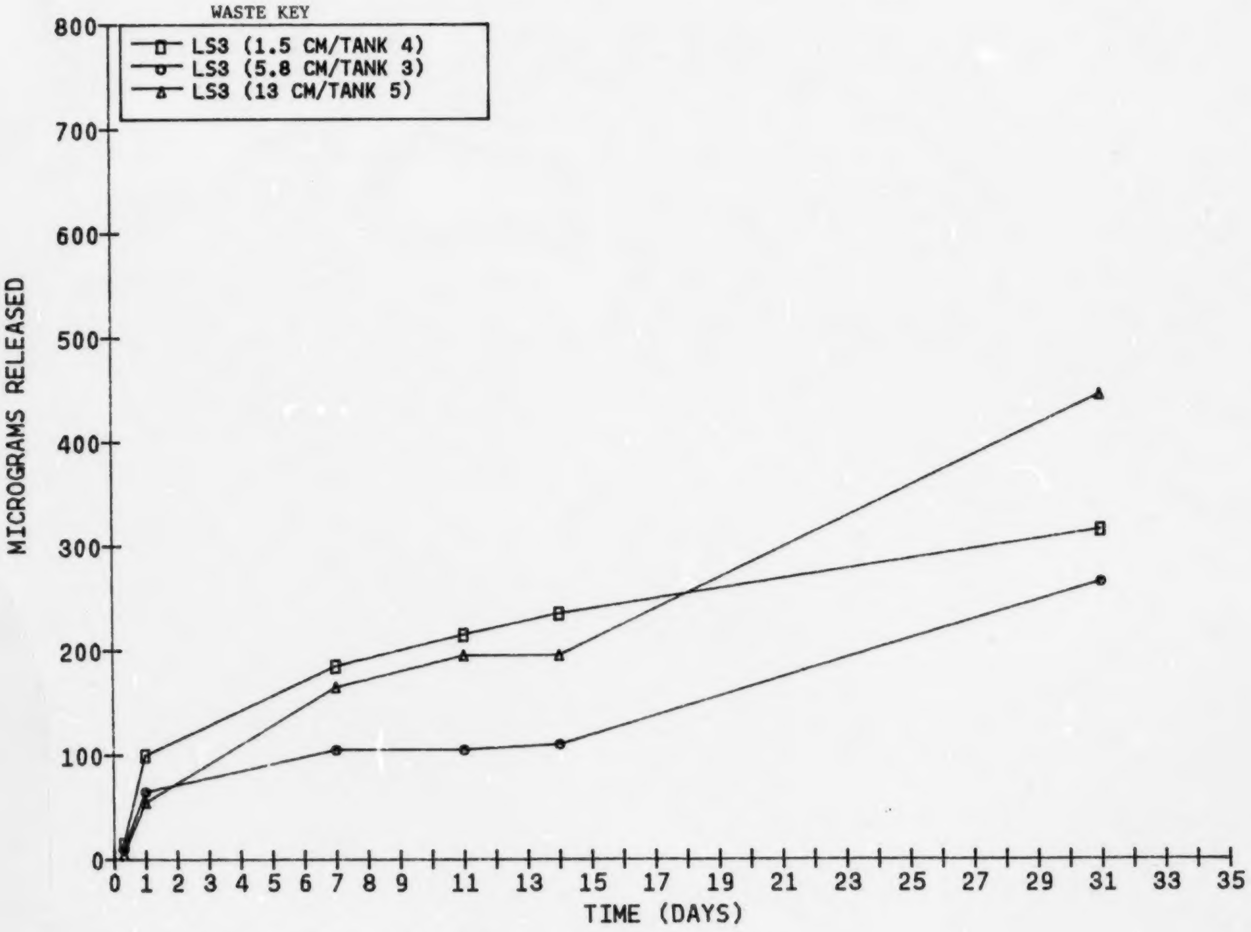
SELENIUM RELEASE (QUIESCENT LEACHING FROM DIFFERENT HEIGHTS)



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 9

CADMIUM RELEASE (QUIESCENT LEACHING FROM DIFFERENT HEIGHTS)



Source; Arthur D. Little, Inc. and New England Aquarium

TABLE 9

RELEASE OF TRACE ELEMENTS FROM FGD WASTES INTO SEAWATER (μg/ℓ) UNDER STIRRED CONDITIONS[a]

Waste	Time of Leach (days)	Zn		Cd		Ni		Se		Hg	
		5%	25%	~5%	~25%	~5%	~25%	~5%	~25%	~5%	~25%
DA1	2	2.8	0.2	0.9	0.1	b	0.1	b	3.4	BDL[c]	BDL
	4	---	---	000	---			5.2	9.3	BDL	BDL
	7	5.8	b	0.5	b	b	b	b	15.8	BDL	BDL
L1	2	1.9	0.7	1.3	0.4	8.0	2.6	46	14	BDL	BDL
	4	---	---	---	---	---	---	40	16	BDL	BDL
	7	4.1	1.5	1.4	0.43	28	3.1	55	23	BDL	BDL
LS3	2	b	1.5	5.7	3.0	0.3	0.6	53	10	BDL	BDL
	4	---	---	---	---	---	---	77	12	BDL	BDL
	7	2.9	2.2	5.0	4.3	3.8	0.84	98	17	BDL	BDL

---

[a] DA1 - 5% slurry had 54 g dry waste and 946 ml seawater.
25% slurry had 124 g dry waste and 876 ml seawater.

L1 - 5% slurry had 63 g dry waste and 937 ml seawater.
25% slurry had 178 g dry waste and 822 ml seawater.

LS3 - 5% slurry had 79 g dry waste and 921 ml seawater.
25% slurry had 274 g dry waste and 726 ml seawater.

[b] No release within detection limits.

[c] BDL = Below detection limit.

Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 10

COMPARISON BETWEEN AMOUNT OF TRACE ELEMENTS RELEASED TO SEAWATER IN STIRRED EXPERIMENT AND THAT PRESENT IN THE SOLIDS

Waste

Element	DA 1			L 1			LS 3		
(% slurry)	μg released	μg present	% released	μg released	μg present	% released	μg released	μg present	% released
Zn (5%)	--	--	--	4.1	370	1.1	2.9	720	0.4
(25%)	--	--	--	1.5	370	4.0	2.2	720	0.3
Cd (5%)	0.5	16	3.1	1.4	50	2.8	5.0	90	5.6
(25%)	BDL	16	--	0.43	50	0.8	4.3	90	4.8
Ni (5%)	BDL	510	--	2.8	2800	1.0	3.8	1400	0.3
(25%)	BDL	510	--	3.1	2800	0.1	0.84	1400	0.1
Se (5%)	BDL	810	--	55	1200	4.6	98	2000	4.9
(25%)	15.8	810	2.0	23	1200	1.9	17	2000	0.9
Hg (5%)	BDL	30	< 0.1	BDL	11	< 0.4	BDL	22	< 0.18
(25%)	BDL	30	< 0.02	BDL	11	< 0.05	BDL	22	< 0.03

BDL = Below Detection Limit.

a = Data for Seven Day Leach.

Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 11

CONCENTRATIONS OF SELECTED TRACE ELEMENTS IN SEAWATER AFTER MIXING WITH FGD WASTE FOR SEVEN DAYS[a]

Waste	Concentration (ppb)				
	Zn	Cd	Ni	Se	Hg
DA1	2 ± 1	0.8 ± 0.4	1.2 ± 0.4	160 ± 20	< 0.04
L1	23 ± 3	3.9 ± 0.7	29 ± 5	210 ± 10	< 0.04
LS3	30 ± 4	40 ± 4	9 ± 1	205 ± 5	< 0.04
Boston Harbor Seawater	10	0.8	1.4	7.7	< 0.04

[a] Equal weight mixture of wet waste and seawater (600 g) (Average of two measurements)

Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 12

LEACHING DATA FOR FGD WASTES UNDER QUIESCENT CONDITIONS[a]

(Total μg Released)

	Tank 1 - DA1				Tank 2 - L1				Tank 3 - LS3				Tank 4 - LS3				Tank 5 - LS3			
Time	Cd	Zn	Ni	Se	Cd	Zn	Ni	Se	Cd	Zn	Ni	Se	Cd	Zn	Ni	Se	Cd	Zn	Ni	Se
4 hrs	BDL	BDL	BDL	BDL	17	BDL	172	---	15	BDL	BDL	---	14	BDL	BDL	---	14	BDL	BDL	---
6.5 hrs	BDL	BDL	BDL	BDL	17	BDL	---		13	BDL	BDL			BDL	BDL		15	BDL	BDL	
1 day	BDL	BDL	BDL	BDL	44	BDL	236		62	BDL	BDL	---	102	BDL	BDL		57	BDL	BDL	---
4 days	BDL	BDL	BDL	BDL	---	BDL	---	3300	---	BDL	BDL	241	---	BDL	BDL	603	---	BDL	BDL	363
7 days	BDL	BDL	BDL	BDL	30	BDL	194	---	103	BDL	BDL	---	185	BDL	BDL	---	166	BDL	BDL	---
9 days	BDL	BDL	BDL	BDL		BDL		2080		BDL	BDL	467		BDL	BDL	648		BDL	BDL	480
11 days	BDL	BDL	BDL	BDL	41	BDL	---	2900	104	BDL	BDL	520	217	BDL	BDL	1091	192	BDL	BDL	1241
14 days	BDL	BDL	BDL	BDL	32	BDL	495	1700	110	BDL	BDL	726	238	BDL	BDL	744	190	BDL	BDL	697
31 days	BDL	BDL	BDL	BDL	45	BDL	324	1700	265	BDL	BDL	814	312	BDL	BDL	1337	446	BDL	BDL	1427
Waste Height:	6.3 cm				6.8 cm				1.5 cm				1.5 cm				13 cm			
Water Volume:	15.1 L				15.1 L				46 L				46 L				30.3 L			
Waste Weight:	∿23,400 g				∿23,400 g				∿6,000 g				∿6,000 g				∿52,000 g			

[a] Total μg released from the waste.

BDL = Below detection limit.

Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 13

COMPARISON OF DATA FROM STIRRED VERSUS QUIESCENT LEACHING EXPERIMENTS

Waste	Element	Leach Time	Stirred	Tank 2	Tank 3	Tank 4	Tank 5
LS3	Se	2 days	10	---	0.8		
Sulfate-rich with ash		4 days	12	---	1	10	0.7
		7 days	17	---	1.7	10	0.8
	Cd	2 days	3.0	---	0.34	2.0	0.23
		7 days	4.3	---	0.44	3.1	0.3
L1	Se	2 days	14	---			
Sulfite-rich with ash		7 days	16	14			
		7 days	23	9			
	Ni	2 days	3	0.6			
		7 days	3	0.8			
	Cd	2 days	1.3	0.07			
		7 days	1.4	0.13			

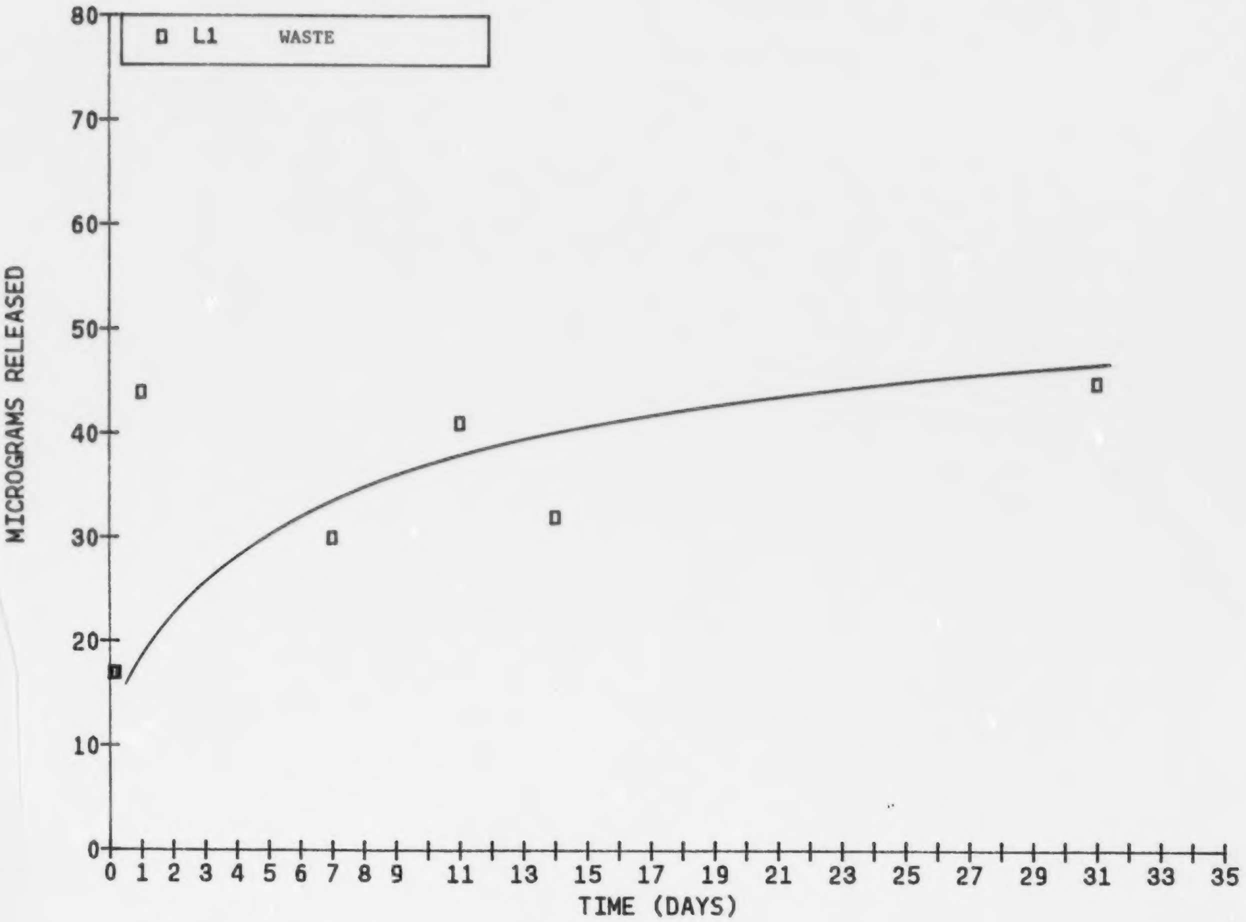
---

[a] Stirred Experiment refers to 25% slurry results. Tanks 2, 3, 4, and 5 were quiescent leaching tanks with 6.8, 5.8, 1.5, and 13 cm of waste on the bottom. The tanks had the same waste surface area exposed to the overlying seawater.

Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 10

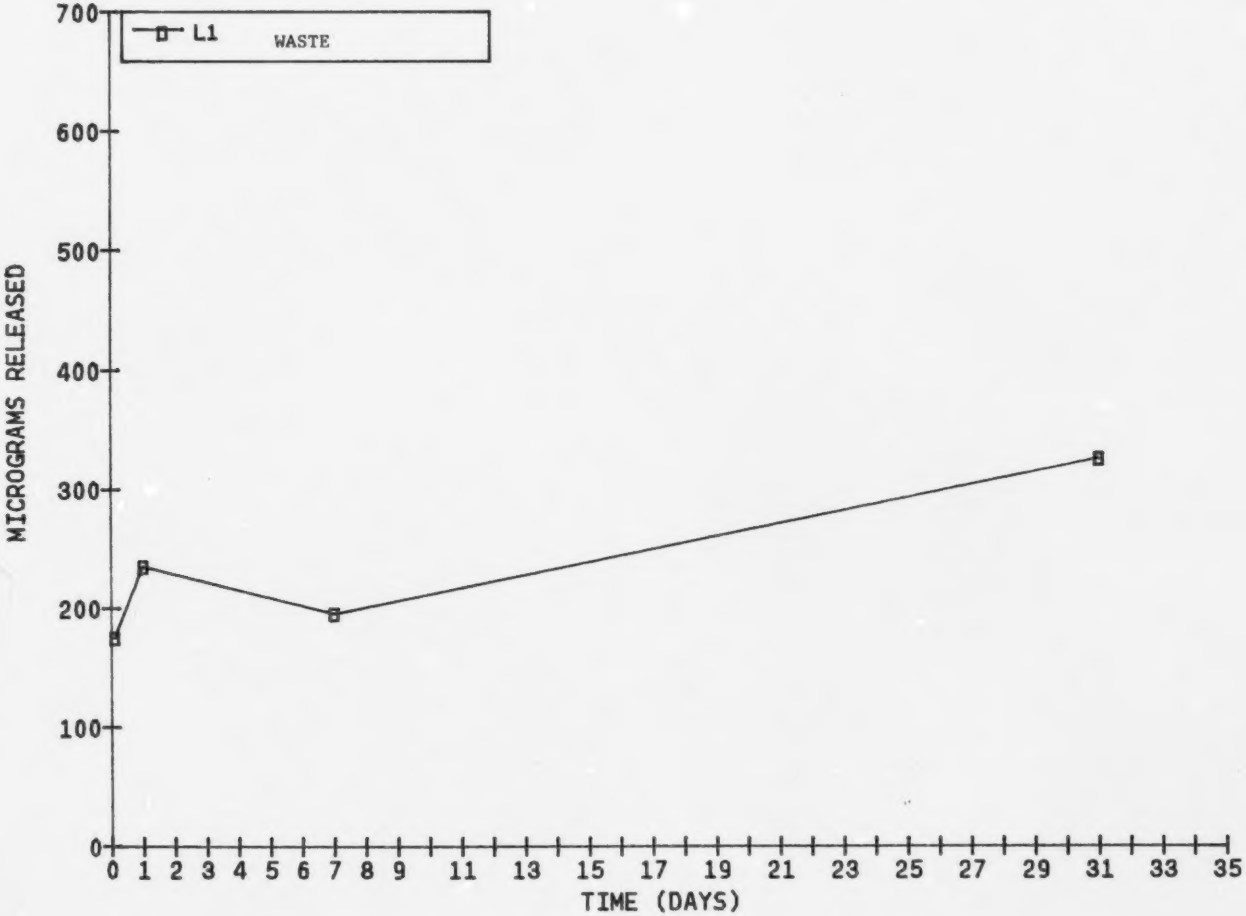
CADMIUM RELEASE (QUIESCENT LEACHING)



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 11

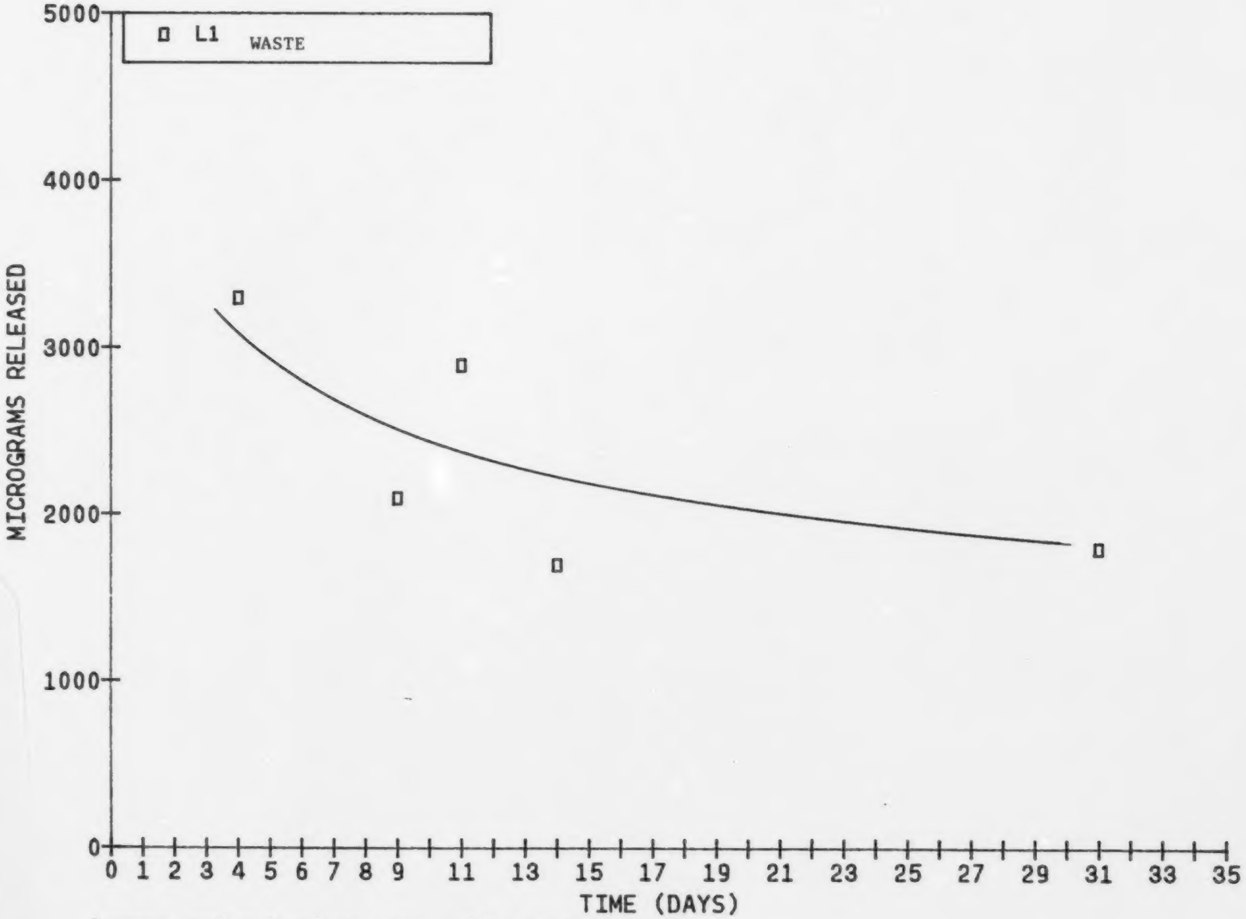
NICKEL RELEASE (QUIESCENT LEACHING)



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 12

SELENIUM RELEASE (QUIESCENT LEACHING)



Source: Arthur D. Little, Inc. and New England Aquarium

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

1.5 cm layer of LS3 material). One way of looking at these data, especially in view of the similarity of results of the Tank 4 quiescent data and the stirred experiment, is to assume that there is little difference between stirred and quiescent leaching for the first 0.5 cm to 1 cm of the waste surface. This may have occurred because the slow mixing of the liquid layer provided some mixing of the waste and seawater or because diffusion allowed an amount leached to mix with the seawater.

The data for the other tanks also suggest that these mechanisms may be involved. As shown in Table 14, the data for Tank 4 suggests diffusion or mixing occurred through one cm of the top of the layer, and a similar calculation for the results in the other tanks yield similar results. Although the values for the waste height leached only agree within a factor of two, it should be noted that the original experimental numbers have gone through extensive manipulations and that the original leach data were not more accurate than that factor for duplication. The correspondence between the calculation of the layer leached in Tank 3 (1.5 cm of total waste height) and in Tank 5 (1.3 cm of total waste height) is supportive of the premise that stirring waste results in little difference in leaching behavior in the surface layer. In addition, the similarity in results obtained using the selenium and cadmium data for the LS3 waste and the Se, Ni, and Cd data for the L1 waste further supports the conclusion.

d. Biological Exposure Tests

(1) Acute and Chronic Toxicity

Based on the results of the acute toxicity tests discussed in Section III A.2 and the preliminary tests described in Section III A.2, there was continuing concern over the potential acute toxicity of the two sulfite-rich test wastes (DA1 and L1). As in the preliminary tests, enough of these wastes were placed as substrates in the test tanks so that waste/organism interactions could have resulted in repetitions of previously observed oxygen depletion and mortality. However, there were no such mortalities among the experimental flounder or clam populations. In fact, no flounder mortalities occurred in any of the test tanks beyond the individuals sacrificed for tissue analysis. As shown in Table 15, four additional deaths of snails (*Littorina*) occurred in one of the test tanks with a sulfite-rich waste substrate. However, in light of the time interval between these deaths, the comparable three deaths in the control tank, and the absence of deaths in the other tank with sulfite-rich substrate, there appears to be no relationship between these four deaths and the sulfite content of the DA1 waste.

The most extensive mortality occurred among the *Zostera* plants, where no individuals in either the control or test tanks survived the exposure period. Because of the complete control tank mortality, it is not feasible to attempt to derive any cause/effect relationships between the presence of the wastes and the lack of surviving plants in the test tanks. NEA observers did note that all the *Zostera* were dead a few days earlier in the DA1 tank (about six days earlier) and exhibited very poor response to this waste substrate throughout the experiment.

For Page Numbering

TABLE 14

CALCULATED THICKNESS OF FGD WASTE LAYER LEACHED DURING QUIESCENT EXPERIMENTS[a]

Waste Sample	Tank[b]	Element	Leaching Time (days)	Layer Thickness Leached (cm)[c]
LS3	4	Se	4	1.2
			7	0.88
	3	Se	2	0.46
			4	0.48
			7	0.58
	5	Se	4	0.75
			7	0.61
			Average	0.71 cm
	4	Cd	2	1.0
			7	1.1
	3	Cd	2	0.64
			7	0.58
	5	Cd	2	1.0
			7	0.91
			Average	0.87 cm
L1	2	Se	7	2.5
		Ni	4	1.3
			7	1.7
		Cd	4	1.1
			7	2.1
			Average	1.7 cm

---

[a] Calculation by comparison of stirred test and quiescent test results.

[b] Waste heights in tanks 2, 3, 4, and 5 were 6.3, 5.8, 1.5, and 13 cm, respectively.

[c] Calculated using μg released per 100 g wet waste for quiescent test divided by μg released per 100 g wet waste in the stirred test multiplied by waste height in tank (cm).

Source: Arthur D. Little, Inc. and New England Aquarium.

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TABLE 15

ANIMAL MORTALITY RECORD
LONG-TERM EXPOSURE TEST

Date	Number	Organism	Tank No.	Waste
July 3	2	Psuedopleurenectes	1	Control
	1	Littorina	8	Control
July 5	1	Mya	6	LS3
	1	Littorina	6	LS3
July 6	4	Mya	6	LS3
July 7	1	Mya	6	LS3
	2	Littorina	6	LS3
July 8	1	Mya	6	LS3
July 11	1	Littorina	5	DA1
July 12	1	Littorina	5	DA1
	3	Littorina	6	LS3
July 20	2	Littorina	6	LS3
	1	Littorina	8	Control
July 21	1	Mya	6	LS3
	1	Mya	overflow tank	LS3
July 24	1	Littorina	6	LS3
	1	Littorina	8	Control
July 25	2	Mya	overflow tank	LS3
July 26	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
July 27	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
August 7	1	Mya	overflow tank	LS3

Source: New England Aquarium

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

A significant, waste-related chronic toxicity response was observed in Tank 6 containing the sulfate-rich LS3 waste and the snails and clams. As shown in Table 15, excessive deaths of individuals of these species occurred in Tank 6 throughout the test until there were no survivors. In an overflow tank established to determine whether Tank 6 or its substrate was causative of the excess mortality, 75% of the exposed organisms (clams) died in two weeks of exposure.

Several possible explanations can be ruled out for the observed toxicity. These include the physical impacts of sedimentation, which were initially suggested by the presence of a large amount of sediment within one of the autopsied clams that died early in the experiment. This high incidence of mortality in the overflow tank as well as the Littorina deaths in Tank 6 indicate that the cause of death was contamination by chemical or biological toxicants present as either very fine particulates or dissolved species. Dissolved oxygen, temperature, and salinity levels remained well within acceptable limits during the tests (see Appendix).

There is strong evidence against attributing the chronic toxicity to the water column levels of any of the four metals monitored during the tests. First, these levels in Tank 6 were comparable to the levels maintained in Tank 3, where no excess deaths occurred with the same organisms and the L1 waste. The respective ranges were as follows (see the Appendix for comparison of individual measurements):

	Ni	Cd	Zn	Se
Tank 6 (LS3)	7-14	9-33	28-45	75-111
Tank 3 (L1)	5-18	8.1-32	17-41	45-106

Note: All values in µg/ℓ.

Second, the levels of the four measured metals in the Tank 6 water column were orders of magnitude below 168 hour LC_{50} and LC_{100} values for snails (Nassarius) and the same species of clam (Mya) for exposure to Cd, Ni, and Zn as measured and reported by Eisler, et al. (1976) (5). The LC_{50} values in µg/ℓ from Eisler's study were as follows:

	Cd	Ni	Zn
Snail	16,000	16,000	7,400
Clam	700	112,000	3,100

Further studies by Eisler involving Mya exposure to complex metal mixtures (including Zn, Ni, and Cd) (6) also suggest that additive toxicity or toxic synergism among the measured metals in Tank 6 is not likely to have caused the observed excess mortality. However, the Eisler data are not considered sufficient to rule out the possibility of synergistic toxicity because lower Cd levels and no Se were involved in his experiments.

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

A more plausible explanation for the Tank 6 results is that the LS3 waste released a form of contamination not measured by the experiment. There are two leading candidates as potential explanations in this context. First, it is quite possible that the waste contained and released a sufficient amount of an unmeasured metal such as copper which proved toxic to the invertebrates in Tank 6. Marine invertebrates including Mya are known to be notoriously sensitive to trace concentrations of copper. Eisler (6) indicated that the copper concentration of 50 µg/ℓ in his complex metals mixure tanks was the leading candidate for the cause of clam mortality in that test. He identified 35 µg/ℓ of Cu as the 168-hour LC_{50} concentration for Mya in the preliminary tests for the referenced experiment. Copper concentrations in FGC wastes have been reported to range up to 100 ppm (4). If the copper concentration in the LS3 waste were in the upper end of this range and its availability for leaching was comparable to that of the "unspiked" Zn in the wastes in the test tanks, then it is quite possible that 20-40 µg/ℓ of copper could have been present in Tank 6 and could thereby have been a cause of or contributor to the observed invertebrate mortalities.

The second candidate explanation is that the LS3 waste released some form of contamination not typically associated with FGC wastes such as some form of organic material. Experimenters working with the LS3 waste reported that the waste was unusually odiferous, substantiating the possibility of organic contamination.

The distinction between these two candidate toxicity explanations is significant. If the toxicity of the LS3 waste is unique, as suggested by the second explanation, it would have far less overall significance than if the toxicity is representative of the toxicity of other sulfate-rich FGC wastes with fly ash. The findings of this study strongly suggest the need for a repetition of the exposure test with a different sample of a sulfate-rich/fly ash waste.

(2) Accumulation of Trace Metals

Cadmium

10 Lines to End of Typing Area

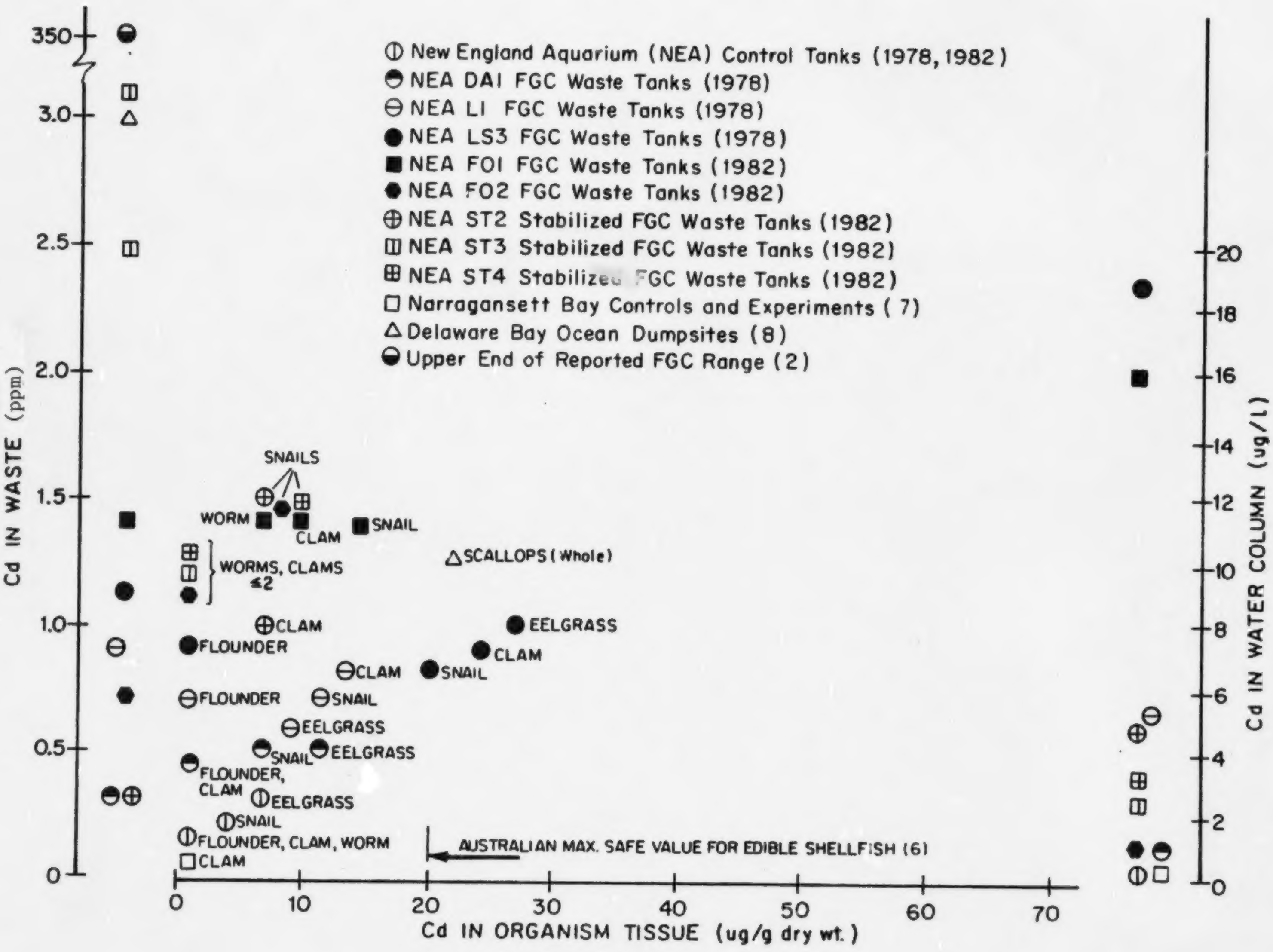
Figure 13 presents a comparison of average values of Cd in the wastes, experimental water columns, and aquatic organism tissues from the NEA tests with FGC wastes. The full set of original data is contained in the Appendix. Also shown are mean Cd values obtained by other investigators in and around the two ocean dump sites off Delaware Bay (7) and in experiments conducted with complex metal mixtures in Narragansett Bay water (6).

In the NEA tests there was clearly a positive correlation between the levels of Cd in the experimental water columns and the levels in the tissues of all the test organisms except flounder. The flounder data are not surprising in light of the findings of other investigations. Several investigations have shown the tendency for Cd concentrations in the low ppb range to accumulate preferentially in specific organs in

For Page Numbering

Figure 13

Cadmium in Wastes, Water Column and Organism Tissue



USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

finfish (i.e., the liver) and therefore to be less subject to detection by the whole-organism sampling methods employed in this series of tests (8).

Note that the concentrations obtained in the invertebrates (especially the clams) are in the same range as those found in shellfish obtained in 1974 from the two existing ocean dump sites off Delaware Bay and the waters around those sites. About 1 billion kg of wastes (combined) were dumped at these sites in 1974, with an average Cd concentration of about 3 mg/kg (wet) (7). This concentration is about three times higher than that measured in the FGC waste highest in Cd for the NEA program, but it is two orders of magnitude below the upper end of the range reported for FGC wastes in general (4). This suggests that further testing of FGC wastes with higher Cd concentrations may be necessary to determine the extent (if any) to which they might create Cd bioaccumulation potentials greater than those of other wastes that continue to be disposed of in the ocean. In that context, it is worth noting that deep ocean sites may continue to be used for industrial wastes like those previously disposed of at one of the dump sites off Delaware Bay (9).

Such a need is reinforced by the NEA test results for the L1 waste in Tank 7. Figure 14 shows the increase in Cd concentrations in Tank 7 clams over the duration of the test and suggests that an equilibrium concentration in tissue had not yet been reached at the time when all organisms had been sacrificed and the test was terminated.

Limited field-scale simulation testing would be an appropriate means to generate the additional data. In such tests there would be no need to maintain Cd concentration artificially at levels corresponding to projected leachates because tank turnover would not be a factor.

Nickel

10 Lines to End of Typing Area

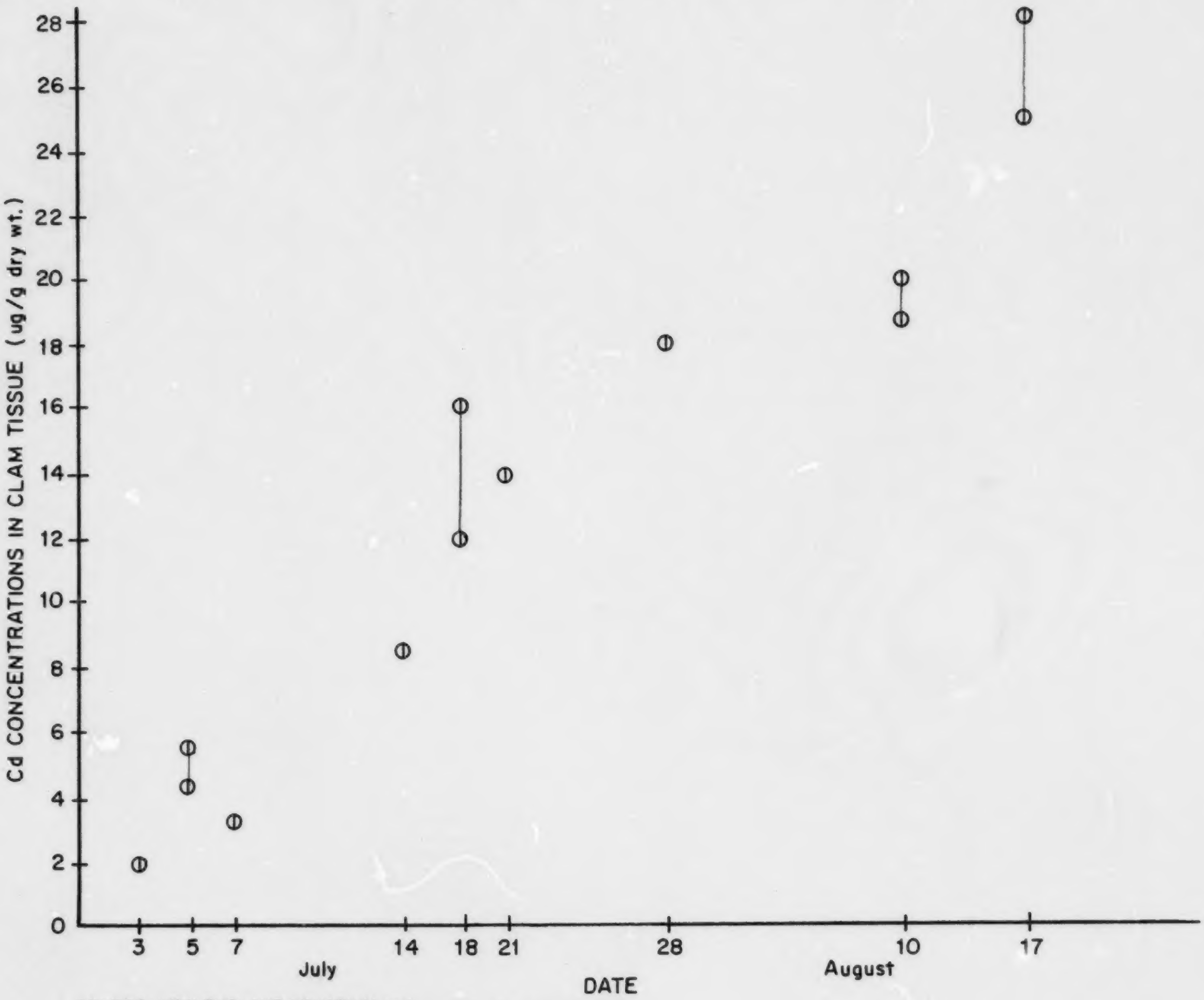
Figure 15 presents a comparison of the waste, water column, and organism tissue levels of Ni measured in the NEA tests along with data reported from other experiments and locations. Values for the tissue concentrations in the NEA tests reflect only data obtained on and after 7/28/78 because prior samples were processed with a blender believed responsible for Ni contamination. Unfortunately, because of the excessive mortalities in Tank 6, no snails or clams remained for processing by 7/28, so that any potential differences in uptake due to exposure to the LS3 waste have not been evaluated.

The data in Figure 15 strongly suggest that Ni leaching and bioaccumulation from ocean-disposed FGC wastes may be a measureable phenomenon but is unlikely to be of environmental significance. Note the rather narrow range (1-15 ppb) of tissue concentrations of Ni despite a broader range of Ni concentrations in wastes (up to almost 40 ppm, wet) and in test water columns (up to almost 60 μg/ℓ). Comparisons of NEA test data with those from Eisler, et al. (6) are particularly interesting, since both experiments used the same organism (Mya arenaria), one set of

For Page Numbering

Figure 14

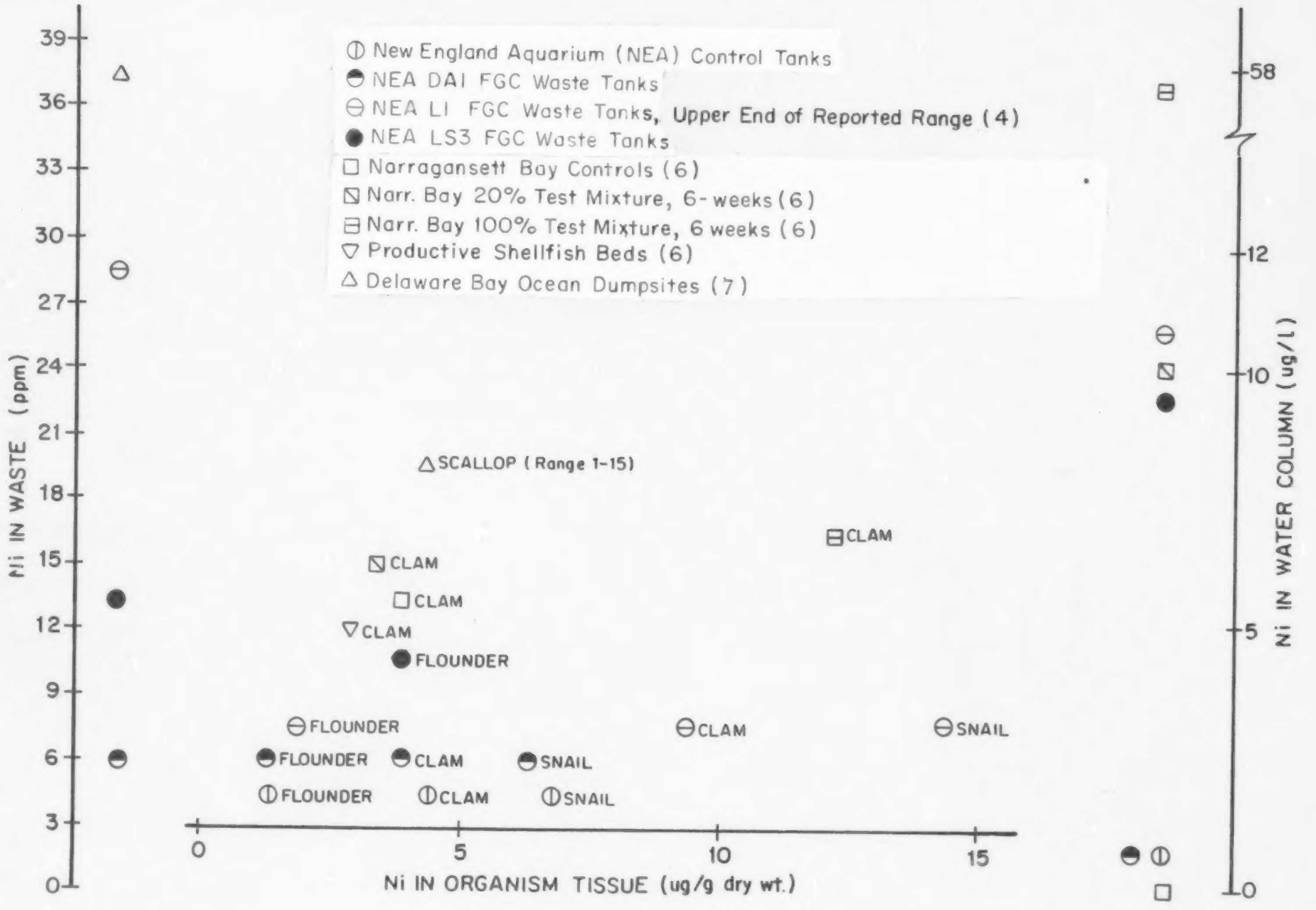
Increase of Cadmium in Clam Tissue in Thirty-Day Test with L-1 Waste



SOURCE: NEW ENGLAND AQUARIUM and ARTHUR D. LITTLE, INC.

Figure 15

Nickel in Wastes, Water Column and Organism Tissue



USE THIS SHEET FOR REPORT TYPING 8 1/2 x 11

TOP

similar Ni water column exposure concentrations (about 10 μg/ℓ), and reported data over the same exposure period (6 weeks). There is excellent agreement between control tissue concentration values between these two experiments as well as between both laboratory experiments and the field data reported for Ni in Mya from healthy shellfish beds by Pringle (6).

It is important to note that the Ni concentrations of the FGC wastes (i.e.,L-1) used in the NEA tests are at the upper end of the reported range for such wastes (4). In the context of Eisler's results (6) showing only slightly higher tissue accumulation upon exposure to Ni concentrations about six times as high (i.e., the 100% test mixture), the results of the NEA tests may represent a reasonable worst case for this contaminant and FGC wastes. Note also that the full-scale ocean dumping of about 1 billion kg/year of wastes with comparable, but somewhat higher, Ni content off the Delaware Bay had resulted in 1974 in shellfish tissue concentrations of Ni in the same range as those determined in the NEA and Eisler tests (6,8).

Selenium

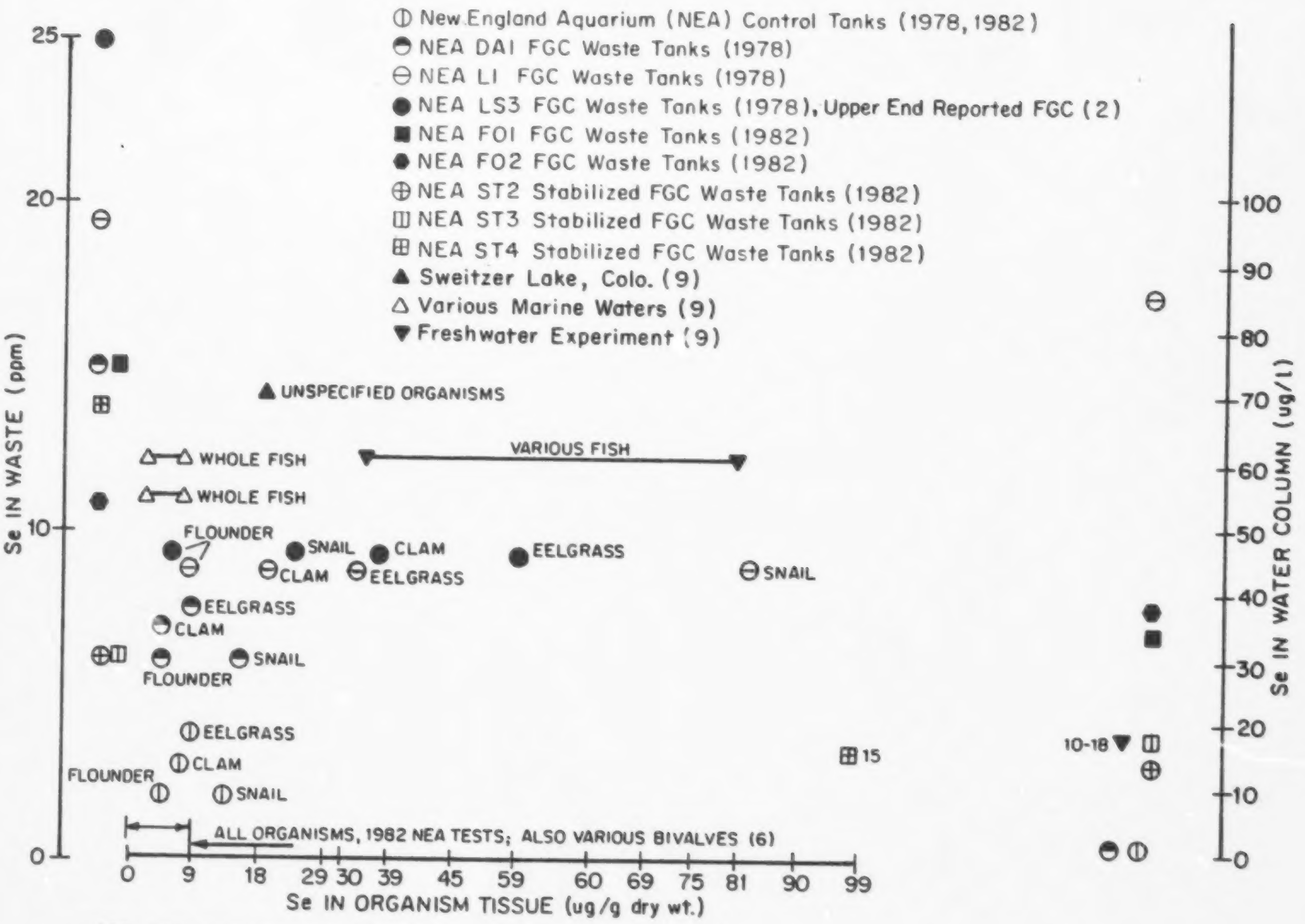
Figure 16 presents a comparison of values for waste, water column, and tissue concentrations of Se for the NEA tests and other reported data. Selenium has been studied far less in marine systems than have the other metals measured in the NEA tests. This creates a poor data base for interpretation of test results. In particular, there appears to be a lack of experimental data against which to evaluate Se accumulation in marine organisms at the water column levels used in the NEA tests. The NEA results and the fresh water data displayed in Figure 16 suggest that there are either some fundamental differences in Se uptake between fresh water and marine fishes or that there may be homeostatic mechanisms favoring elimination over accumulation upon exposure to Se concentrations in the 100 μg/ℓ range.

There appears to be good agreement between the tissue concentrations of Se in the NEA control tanks and tissue concentrations reported for various marine bivalves and finfish from field studies around the world. However, the experimental data for the LS3 and L1 FGC wastes show higher accumulation levels than previously reported for marine organisms. It should be remembered that the analytical protocol for Se determination in the NEA tests gave sufficiently irregular results to merit extreme caution in their interpretation. Nonetheless, there appears to have been a positive correlation between the presence of the elevated Se levels in the LS3 and L1 FGC waste test tanks and the accumulation of Se in the test organisms.

The water column level of Se in the 100 μg/ℓ range that prevailed in the NEA tests correspond to levels judged to represent potential danger in Sweitzer Lake, Colorado (10). Because so little is known about Se and its effects on marine organisms and because Se is an important trace constituent of many FGC wastes (with and without fly ash), it appears appropriate to continue to investigate this parameter in further experimental work, particularly at limited field scale. The Se content of the

Figure 16

Selenium in Wastes, Water Column and Organism Tissue



NOTE: DETECTION LIMIT VALUES USED AT 1/2 FACE VALUE (eg. <20=10)

LS3 waste was measured to be at the upper end of the reported range for FGC wastes (4), so that further work with this or an analogous waste would be appropriate.

Zinc

Figure 17 presents a comparison of Zn concentrations measured in FGC wastes, water, and organisms in the NEA tests along with data collected by others in other locations. Again, the six-week Narragansett Bay water tests with *Mya* by Eisler, *et al*. (6) provide an interesting framework for comparison. In this instance, Eisler's 20% and 100% solutions created exposure to sublethal water column zinc levels about 20-100 times higher than those in the NEA FGC waste tests. Note also that the Zn levels reported for the billion kg of wastes dumped in the ocean off the Delaware Bay in 1974 (7) correspond very closely to the upper end of the range verified for the LS3 FGC waste in the NEA tests. This waste had the highest reproducible zinc concentrations of those tested, although some measurements showed levels up to about three times as high for the DA1 waste.

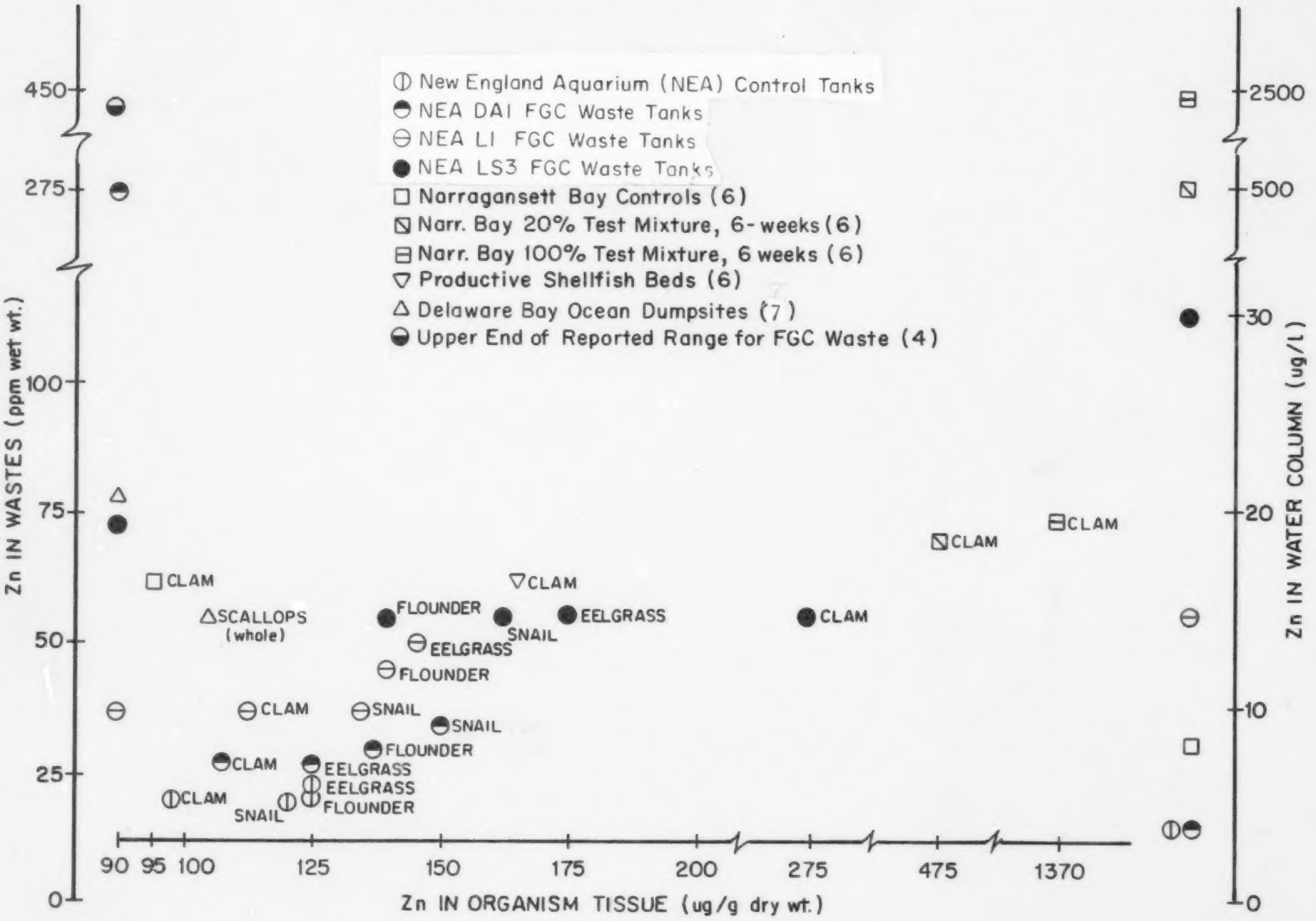
Reported accumulation of Zn in various organisms under control conditions in the laboratory, in "productive shellfish beds" (6), and at and around the Delaware Bay ocean dump sites (7) correspond closely to the 100-200 μg/g levels observed in the control and three of the four experimental FGC waste systems used in the NEA tests. These results suggest that Zn leachate and accumulation is unlikely to be a problem if these or similar FGC wastes were to be ocean dumped. The NEA data and the work of others do suggest a positive correlation between Zn waste, water column, and organism concentrations even for the NEA invertebrate tanks with the DA1 and L1 wastes where little or no artificial subsidy of water column Zn levels was practiced. The upper end of the range of Zn-rich FGC wastes was apparently not fully represented by the wastes used in the NEA tests (4).

If zinc-rich FGC wastes were to leach proportionate amounts of Zn to those already tested, one would expect accumulation results to fall between those illustrated in Figure 17 for the LS3 waste and Eisler's 20% metals mixture. Such levels would be two to three times higher than the range of control values and would be unlikely to approach the potential toxic thresholds represented by Eisler's 100% mixture.

As in the Cd exposure situation, finfish Zn values measured in the NEA tests are likely not to reflect the preferential concentrations of Zn in certain organs, especially the liver. Mears *et al*. (11) found liver Zn concentrations averaging an order of magnitude higher than those in the whole tissue samples from the NEA tests. Their analyses were performed on several species collected from the southern part of the New York Bight.

Figure 17

Zinc in Wastes, Water Column and Organism Tissue



USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

IV. SUMMARY EVALUATION OF ENVIRONMENTAL IMPACT POTENTIALS

Based on the findings of the three phases of work in this program, summary evaluations of potential environmental impacts of at-sea disposal of unstabilized FGC wastes are presented below.

A. BENTHIC SEDIMENTATION IMPACTS

The field observations and experimental results from the later portions of this program have both legitimized initial concerns about potential benthic sedimentation impacts, and suggested means of impact mitigation or avoidance.

The field observations made near Key West during the refined assessment (2) showed that at least one type of FGC waste substrate appeared substantially less capable of supporting diverse marine benthic communities than did the other neighboring sediments. However, a year later, when the FGC waste substrate had been covered by and mixed with other local sediments, benthic community recovery appeared to be in progress.

In the thirty-day exposure tests during this phase of the program, excessive mortalities of finfish and invertebrates provided examples of chemical, but not physical liabilities of concentrations of certain FGC wastes as marine substrates. In these instances, respectively, substrate-derived chemical impacts in the forms of sulfite-related oxygen depletion and trace element contamination made the substrate unsuitable, as discussed below. The significance, if any, of the failure of eelgrass (*Zostera*) to adapt to any of the FGC substrates in the exposure tests cannot be evaluated, because the species also failed to adapt to the control substrates. Flounder apparently adapted successfully to the 2% sulfite-rich unstabilized waste substrate that was used in the thirty-day exposure tests. All test animals appeared to adapt successfully in tanks where only small patches of sulfite-rich FGC waste substrate were present. However, the degree and importance of voluntary avoidance should be further investigated.

10 Lines to End of Typing Area

In summary, it appears that the dispersed disposal of FGC waste at sea would provide a reasonably sure means of avoiding potentially adverse physical benthic sedimentation impacts. It is expected that adequate dispersal and mixing with local sediments would be relatively easy to achieve in the deep ocean, but would require careful disposal site designation and management on the continental shelf.

B. SUSPENDED SEDIMENT IMPACTS

The results of the acute toxicity testing in this program indicate that there are unlikely to be significant differences between the ocean water

For Page Numbering

column impact potentials of descending masses of sulfate-rich FGC wastes and the comparable water column impacts presently experienced and accepted for ocean disposal of various clean dredged materials. However, without adequate dispersal, descending masses of unstabilized sulfite-rich FGC wastes could create opportunities for organism exposure to toxic/anoxic conditions in the water column.

This program did not experimentally investigate the potential water column implications of descending FGC wastes at field scale, nor the implications of descending FGC wastes high in trace contaminants. The modelling efforts in the refined assessment (2) suggested a possible need for further evaluation of the potential for existence and avoidance of water concentrations in excess of the levels that subsequently proved toxic. The toxic effects of water column leachates from the LS3 waste in the thirty-day exposure tests require further investigation to determine whether in special circumstances (i.e., for highly or uniquely contaminated FGC wastes), water-column toxicity during the descent of a sulfate-rich waste can be ruled out.

As in the case of potential benthic sedimentation impacts, dispersed disposal requirements appear to be a promising means for eliminating potential adverse impacts from suspended FGC wastes during descent through the ocean water column.

C. SULFITE-RELATED OXYGEN DEPLETION

Initial concerns over the potential adverse effects of sulfite-related oxygen depletion were confirmed by the experimental work in the later phases of this program. The acute toxicity tests and the preliminary long-term exposure experiments indicated that anoxic conditions could be created that would result in complete organism mortality in the presence of unstabilized sulfite-rich FGC wastes. In that context, the preliminary exposure experiments with flounder are more significant, because they represented voluntary interaction between the organisms and the waste substrate in the absence of supplementary agitation.

The later preliminary flounder exposure experiments and the thirty-day exposure tests with sulfite-rich wastes demonstrated that circumstances can be created where sulfite-related oxygen depletion and toxicity are avoided. Because sufficient amounts of waste were also present in these later tests to have created oxygen depletion and toxicity, there is the suggestion that voluntary avoidance may be practiced where sufficient non-waste substrate is available. If this is true at field scale, then dispersed ocean disposal may be an acceptable means of avoiding sulfite-related toxicity.

D. TRACE CONTAMINANT IMPACTS

The dissolution, leaching, and long-term exposure test results provided a mix of positive and negative implications concerning potential trace contaminant impacts. On the positive side, these tests provided strong evidence that there are not likely to be significant, incremental effects from the release of some FGC waste trace contaminants that were initially of concern. Specifically, this appears to be the case for Ni and Zn, both of which were initially of concern because of their inherent toxicity and their widespread presence in FGC wastes.

On the negative side, there is the contamination-related toxicity observed in the invertebrate exposure tests with the unstabilized sulfate-rich LS3 waste. It is important to establish whether or not the observed toxicity was uniquely associated with a contaminated sample of the particular waste, or whether it is a phenomenon that would be expected with similar FGC wastes under normal circumstances.

Results for other trace contaminants, notably Cd and Se, are inconclusive. For these substances, either too little is known in general (Se) or the program may not have tested highly-contaminated wastes (Cd). Overall, there is an apparent need and direction for further investigation of remaining trace contaminant impact potentials.

V. CONCLUSIONS

The two overall conclusions of the initial assessment (1) are still considered valid. These conclusions, which emphasize the need for case-by-case analyses of prospective ocean disposal of FGC wastes, and affirm the technical feasibility of four available control options, are contained in their entirety in Section II. A of Part One of this report. More specific conclusions considered appropriate based upon the testing and assessment to date are as follows:

- The concentrated disposal of unstabilized FGC wastes with soil-like physical properties in the ocean still appears to be environmentally undesirable because of potential benthic sedimentation impacts, and, for sulfite-rich wastes, potential sulfite-related oxygen depletion. Further work may contradict this conclusion.
- The problems of disposal of sulfite-rich FGC wastes still appear considerable. However, the technically feasible degree of dispersal during dumping operations now appears to be a potentially useful control option for mitigation of potential oxygen depletion impacts.
- The potential release and accumulation of nickel and zinc from ocean disposal of unstabilized FGC wastes does not appear likely to constrain ocean disposal of these wastes.
- The release of other trace contaminants remains a potentially valid concern that could preclude ocean disposal of FGC wastes.
- Disposal options which appear promising and are recommended for further research include:
    - dispersed disposal of all forms of FGC wastes on the continental shelf or in the deep ocean; and
    - concentrated disposal of stabilized, brick-like FGC wastes on the continental shelf or in the deep ocean.
- Concentrated (conventional) disposal of unstabilized, sulfate-rich FGC sludges in the deep ocean may be promising, and should be reconsidered after further testing of the chronic toxicity of different samples of such wastes.

USE THIS SHEET FOR REPORT TYPING 8 1/2 x 11

TOP

VI. RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The following research needs were believed important upon completion of the investigations described in Part One of this report:

- Further empirical bioassay data on the acute and chronic effects of ash-rich, sulfate-rich FGC wastes, using test organisms found sensitive to one such waste in this program.

- Further laboratory-scale leaching and bioassay data on the availability and effects of selected trace contaminants in FGC wastes, including Cd, Se, Cu, and possible organic trace contaminants.

- Limited field-scale tests to investigate the importance of

  (1) avoidance responses as potentially mitigative of sulfite-related toxicity; and

  (2) trace contaminant uptake under representative conditions for leaching and water exchange.

- Parallel data on stabilized FGC materials in the above subject categories; and

- Continual investigations of any full-scale field situations where FGC wastes have entered or been placed in marine environments.

10 Lines to End of Typing Area

For Page Numbering

VII. REFERENCES

1. Lunt, R. R., C. B. Cooper, S. L. Johnson, J. E. Oberholtzer, G. R. Schimke, and W. I. Watson, 1977. "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," EPA 600/7-77-051, U.S. Environmental Protection Agency, Office of Research and Development.

2. Lunt, R.R., C.B. Cooper, A.S. Reyman, S.L. Johnson, I. Bodek, W.I. Watson, (Arthur D. Little, Inc.) and G.C. McLeod, A.J. Barker, (Edgerton Research Laboratory, New England Aquarium), "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Refined Assessment." Report to U.S. Environmental Protection Agency, Office of Research and Development under Contract No. 68-03-2334, 1981.

3. Sherk, J. A., J. S. O'Connor, and D. Neumann, "Effects of Suspended and Deposited Sediments on Estuarine Organisms, Phase II." Final Report, University of Maryland, Department of Environmental Research, Chesapeake Biological Laboratory, 1974.

4. Santhanam, C. J., R. R. Lunt, C. B. Cooper, D. E. Kleinschmidt, I. Bodek, and W. A. Tucker (Arthur D. Little, Inc.), and C. R. Ullrich (University of Louisville), "Waste and Water Management for Conventional Coal Combustion, Assessment Report--1979," EPA 600/7-80-012, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, 1980.

5. Eisler, Ronald and Raymond J. Hennekey, "Acute Toxicities of Cd^{2+}, Cr^{+6}, Hg^{2+}, Ni^{2+} and Zn^{2+} to Estuarine Macrofauna," EPA-600/J-77-151, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

6. Eisler, Ronald and Raymond J. Hennekey, "Toxicity Evaluation of a Complex Metal Mixture to the Soft Shell Clam (Mya arenaria)," EPA-600/J-77-149, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

7. Reynolds, Bruce H., "Trace Metals Monitoring at Two Ocean Disposal Sites," EPA-600/3-79-037, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1979.

8. Cooper, C. B., Sara E. Bysshe, Leslie Nelken, Kate Scow, and William Tucker, Arthur D. Little, Inc., "Risk Assessments of Priority Pollutants: Cadmium, Second Draft," Prepared for U.S. Environmental Protection Agency, Monitoring and Data Support Division, Washington, D.C., April, 1979. (Unpublished)

9. U.S. Environmental Protection Agency, "Draft Environmental Impact Statement (EIS) for 106 Mile Ocean Waste Disposal Site Designation," Prepared under Contract 68-01-4610, for U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Marine Protection Branch, Washington, D.C., T. A. Wastler, Project Officer; 1979.

10. Birkner, John H., "Selenium in Aquatic Organisms from Seleniferous Habitats," AFIT Report No. Ci-79-34D, Defense Documentation Center, Defense Logistics Agency, Cameron Station, Alexandria, Virginia, 1978.

11. Mears, Harold C. and Ronald Eisler, "Trace Metals in Liver from Bluefish, Tautog and Tilefish in Relation to Body Length," EPA-600/J-77-148, University of Rhode Island, Department of Zoology, Kingston, Rhode Island, and U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

20 Lines to End of Typing Area

For Page Numbering

ADL 054 1279 200M

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Appendix A: Acute Toxicity Testing

Excerpted from Progress Report #1 by Albert J. Barker, Edgerton Research Laboratory, New England Aquarium to Arthur D. Little, Inc.

Description of the Suspension Tanks for the LC_{50} Bioassay on Menidia menidia

The entire test apparatus is shown in Figure 1. The setup consists of seven hemispherical suspension tanks and one rectangular 80-liter aquarium. All of the tanks are made of fiberglass and will hold a maximum of 80 liters. The tanks in the foreground contain the makeup test suspensions and the control seawater that feed the test and control tanks in the background (the rectangular tank containing only seawater for the control test need not be suspended). Three different concentrations of a given sludge plus the control can be run at the same time. Water from the makeup tanks is pumped into the test tanks at a flow rate equivalent to overturn five test tank volumes in 24 hours.

Figure 2 shows the pumping mechanism that keeps the sludge in suspension. The intake side of the pump draws water from the side of the tank and pumps it back in at the bottom in a continuous cycle (each of the suspension tanks contains a circulating pump). Inside the test suspension tanks at the bottom (see Figure 3) the incoming water from the pump hits a dispersion funnel that forces the water down and up the sides of the tanks. This action prevents any of the particulates from settling out. The intake manifold reduces the intake velocity of the pump, so the fish do not get sucked against it. The makeup water line introduces the suspensions at the bottom of the test tank, and the displaced suspension flows out the standpipe. This keeps the volume in the test tanks the same throughout the test period.

10 Lines
to End of
Typing Area

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TOXICITY STUDIES:

PHASE III, OCEAN ASSESSMENT

ADL Case No. 78521-04

Progress Report #2

by

Albert Barker and Thomas Gilbert
Edgerton Research Laboratory
New England Aquarium

to

Arthur D. Little, Inc.

10 Lines
to End of
Typing Area

For Page Numbering

ADL 054-12/78-300M

INTRODUCTION

This report describes the status of tests measuring the toxicity of sludges L2 and LS2 on *Menidia menidia* and *Acartia tonsa*. Modifications to the testing program and the time course for the remainder of the study are described.

SECTION I: Definitive Bioassay of L2 and LS2 on *Menidia menidia*

A. PROCEDURES

A total of 20 fish, averaging 0.8 g in weight and 5.5 cm in length, were used for each of the test concentrations and the control. The fish were kept in holding tanks for a period of one month and were randomly selected for testing. At the beginning of the 96-hour tests a weighed amount of sludge was added to both the test and makeup suspension tanks (a description of test apparatus was given in Progress Report #1). Metering pumps delivered the sludge from the makeup tanks, into the test tanks, at a rate equivalent to five test tank volume changes in 24 hours. During the test, weighed amounts of the test sludge were added to each makeup tank at approximate 24-hour intervals.

During these tests, several chemical analysis procedures were modified. Dissolved oxygen was measured polarographically rather than by the Winkler titration used previously. The Winkler method (even with the $CuSO_4^-$ sulfamic acid modification) was found to suffer from a sulfite interference. At pH 7.5-8.0 sulfite does not appear to affect the membrane electrode measurement.

Total suspended solids (TSS) were measured by centrifuging 4-5 liters of suspension from the makeup tanks rather than the test tanks because of the smaller volume (20 ℓ) in the latter. The centrifuged solids were dried, weighed, and then subdivided for total oxidizable sulfur (TOS) and calcium measurements. In test #4 there was insufficient sample to measure Ca. Representatives of Arthur D. Little suggested that TSS measurements be done by measuring total and dissolved calcium concentrations.

The method for calcium measurement has also been revised. An evaluation of the plasma emission technique used at New England Aquarium indicated that even samples diluted 1:100 were influenced by self-absorption in the plasma arc. However, this interference is not as severe for the Ca ionized spectral line at 2968 Å. Therefore, all seawater samples are to be diluted and analyzed at this wavelength. To achieve greater analytical precision, the "blank" solution against which each sample is measured will be diluted, filtered seawater. In this way a sort of differential measurement will be made which should improve long-term precision.

Representatives of Arthur D. Little requested that the L2 definitive LC_{50} test be redone using a nitrogen purge in the makeup tanks. It was felt that this procedure would subject the fish to higher sustained levels of sulfite. The test was conducted in the same manner as the others except that the makeup water was deoxygenated prior to the addition of the sludge. The makeup tanks were covered with a plexiglass sheet, and nitrogen was bubbled in throughout the test. The results showed substantially higher levels of sulfite. However, the LC_{50} value did not change, suggesting that the toxic response is a function of the immediate oxygen demand.

At the request of Arthur D. Little staff, larger pumps were purchased to suspend higher concentrations (above 10,000 ppm) of the G1 sludge. A 96-hour control test was conducted to determine if the fish could withstand the higher turbulence. During the test, 15% of the fish died. This mortality is slightly above the maximum allowed for a control situation. In spite of this, we have decided to run a definitive bioassay on the G1 since the equipment is set up and some useful information may be derived from the test.

B. RESULTS

LC_{50} plots and raw data for all tests are given in Exhibit 1.

SECTION II: Effects of L2 and LS2 on Acartia tonsa

A. PROCEDURES

A total of 60 adult organisms divided into four groups of 15 each were used in each test. Each group was placed in a 300 cc capacity crystallization dish containing 200 cc of filtered seawater. A fifth dish containing the test medium but not necessarily test organisms, was also set up. From this dish, water samples were periodically taken for chemical analysis. The dishes were mildly agitated on a rotary shaker table during the testing period. A 2000 ppm slurry of each test sludge was prepared in oxygen-free seawater. Aliquots of slurry were added to the test dishes.

For these tests the usual array of chemical measurements was modified somewhat on the recommendation of Arthur D. Little staff. TOS was not measured because of the small quantity of sample. The calcium concentration of aqueous and particulate phases was used to indirectly estimate TSS levels. The results of the calcium measurements will be included in the next progress report.

B. TEST RESULTS AND EXPERIMENT MODIFICATION

The results of the range-finding tests indicated that for the L2 sludge the lethal concentration is between 200 and 400 ppm; LS2 value is between 450 and 600 ppm (raw data for both the range-finding and definitive tests are given in Exhibit 2).

A definitive test on the L2 sludge was started but then terminated for the following reasons:

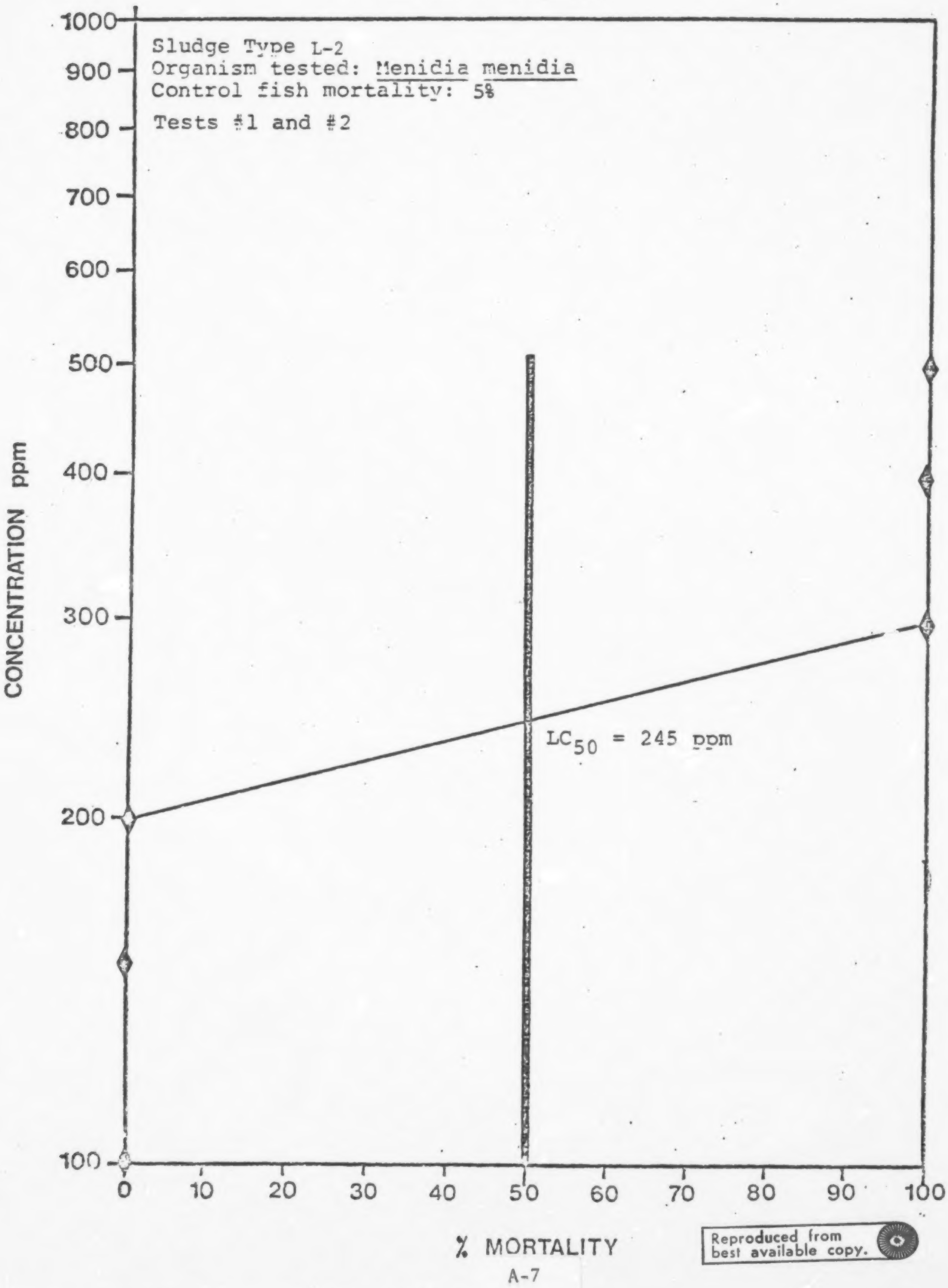
1) More than the acceptable number of control organisms were dying.

2) Arthur D. Little staff felt the test apparatus did not sufficiently subject the organisms to suspended concentrations of the sludge. A new testing scheme was devised and is being evaluated. In the new procedure, 60 _Acartia_ will be placed in 1-liter capped bottles completely filled with test media. Sludge concentrations will be added as an accurately weighed solid rather than from a concentrated slurry. The bottoms will be inverted every 15 minutes over an eight-hour period and then left standing overnight. This procedure will be repeated every day over the 96-hour testing period. Sampling and counting of the organisms will be conducted only at the beginning and end of the test. This procedure should substantially extend the time the copepods are subjected to suspended concentrations of the sludge. If the organisms survive the new testing scheme, this procedure will be immediately started for the definitive LC_{50} 96-hour bioassay.

The G1 sludge may present another problem if range-finding tests show that the toxic levels are in the 10,000 to 20,000 ppm range. With loadings this high, it will be virtually impossible to see (let alone count) the _Acartia_ in the test bottles.

Exhibit 1

96 HOUR BIOASSAY



Reproduced from best available copy.

96 HOUR BIOASSAY

Experiment Number: 1 **Species:** Menidia menidia **No. of Organisms:** 20/test and 20/control
Sludge Type: L-2 **Sludge Concentrations:** A 100 ppm B 150 ppm C 200 ppm

Test Started: 11:00 AM. **Date:** 27 June 1977.

	Makeup Addition Time	T °C	Sal. ‰	Dissolved Oxygen, mg/l			NH_3 µgN/l	T.S.S. mg/l	$SO_3^=$ x10^{6}m/l	# Dead Animals	T.O.S. mmoles/g	Ca mmoles/g	Ca/T.O.S.
Sampling Time		0.0	0.0	0.1	0.5	5.0			0.7			3.0	
Control		20.0	31.0	7.6	N.D.	7.5				0			
A		20.0	31.0	1.9	2.5	6.1		1.9	653	0	0*	0.89±0.01	
0 Hr B		20.0	31.0	0	1.8	6.6		1.7	426	0	0*	0.93±0.01	
C		20.0	31.0	0	0	6.1		2.6	482	0	0*	0.90±0.03	
Sampling Time		22.0	22.0	23.0			23.5		24.0				
Control	22.0	22.0	30.0	8.2			70		0	0			
A		22.0	30.0	8.1			378	1.2	31	0			
24 Hr B		22.0	31.0	8.4			616	1.3	25	0			
C		22.0	31.0	7.0			560	2.8	28	0			
Sampling Time		45.0	45.0	46.0					52.0				
Control	46.0	20.0	30.0	8.0					0	0			
A		20.0	30.5	8.6				1.4	0	0			
48 Hr B		20.5	30.5	8.7				1.2	0	0			
C		20.5	31.0	9.3				2.8	0	0			
Sampling Time		69.0	69.0	69.0					74.7				
Control	69.7	21.0	30.0	7.4					0	0			
A		20.0	31.0	8.7				1.5	0	0			
72 Hr B		21.0	30.0	8.6				2.3	0	0			
C		22.0	30.0	7.4				2.5	16	0			
Sampling Time		94.0	94.0	94.0			94.5		95.7			96.0	
Control	93.7	19.5	31.0	9.1			98		0	0			
A		19.5	31.5	7.2			490	8.7	0	0	0*	1.42±0.01	
96 Hr B		19.8	31.5	7.3			364	10.1	43	0	0*	1.27±0.01	
C		20.0	31.5	7.4			364	13.3	21	0	0*	1.28±0.01	

*Below detection limit

96 HOUR BIOASSAY

Experiment Number: 2
Sludge Type: L-2

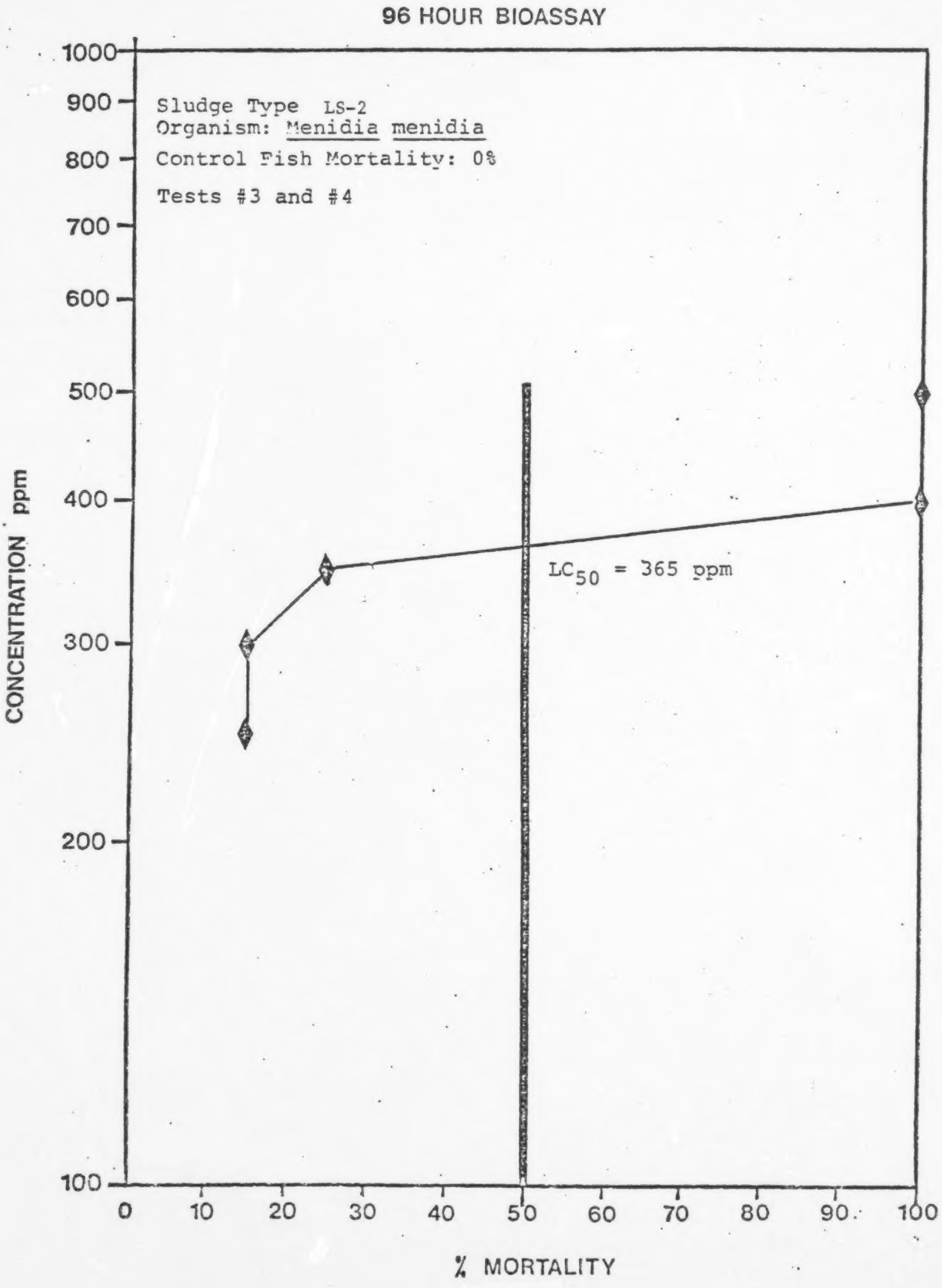
Species: Menidia menidia
Sludge Concentrations: A 300 ppm B 400 ppm C 500 ppm

No. of Organisms: 20/test and 20/control

Test Started: 08:30 AM. Date: 5 July 1977

		Makeup Addition Time	T °C	Sal. ‰	Dissolved Oxygen, mg/l				NH_3 µgN/l	T.S.S. mg/l	$SO_3^=$ x10⁶m/l	# Dead Animals	T.O.S. mmoles/g	Ca mmoles/g	Ca/T.O.S.
Sampling Time			0.0	0.0	0.1						0.8	0.6		3.0	
Control			20.0	30.5	7.3						0	1			
	A		19.5	31.0	0					5.2	803	20	0*	0.97±0.01	
0 Hr	B		19.5	31.0	0.7					6.2	538	20	0.35	1.61±0.01	4.6
	C		19.5	30.5	0					9.1	1435	20	0.15	3.10±0.06	20.6
Sampling Time															
Control															
	A														
24 Hr	B														
	C														
Sampling Time															
Control															
	A														
48 Hr	B														
	C														
Sampling Time															
Control															
	A														
72 Hr	B														
	C														
Sampling Time															
Control															
	A														
96 Hr	B														
	C														

*Below detection limit


96 HOUR BIOASSAY
Sludge Type LS-2
Organism: Menidia menidia
Control Fish Mortality: 0%
Tests #3 and #4
LC$_{50}$ = 365 ppm
CONCENTRATION ppm
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
80
90
100
% MORTALITY

96 HOUR BIOASSAY

Experiment Number: 3
Sludge Type: LS-2

Species: Menidia menidia
Sludge Concentrations: A -- B 400 ppm C 500 ppm

No. of Organisms: 20/test and 20/control

Test Started: 14:25 AM. **Date:** 5 July 1977

	Makeup Addition Time	T °C	Sal. ‰	Dissolved Oxygen, mg/l	NH_3 µgN/l	T.S.S. mg/l	$SO_3^=$ x10^{-6}m/l	# Dead Animals	T.O.S. mmoles/g	Ca mmoles/g	Ca/T.O.S.
Sampling Time		0.1	0.1	0.2	0.8		0.4			3.0	
Control		19.0	31.0	7.4	210		0	0			
A		-	-	-	-	-	-	-	-		
0 Hr B		19.5	31.0	0	210	89.3	1465	20	3.71	3.8±0.1	1.02
C		19.5	31.0	0	238	116.2	1605	20	3.41	3.4±0.1	1.00
Sampling Time											
Control											
A											
24 Hr B											
C											
Sampling Time											
Control											
A											
48 Hr B											
C											
Sampling Time											
Control											
A											
72 Hr B											
C											
Sampling Time											
Control											
A											
96 Hr B											
C											

96 HOUR BIOASSAY

Experiment Number: 4
Sludge Type: LS-2

Species: Menidia menidia
Sludge Concentrations: A 250 ppm B 300 ppm C 350 ppm

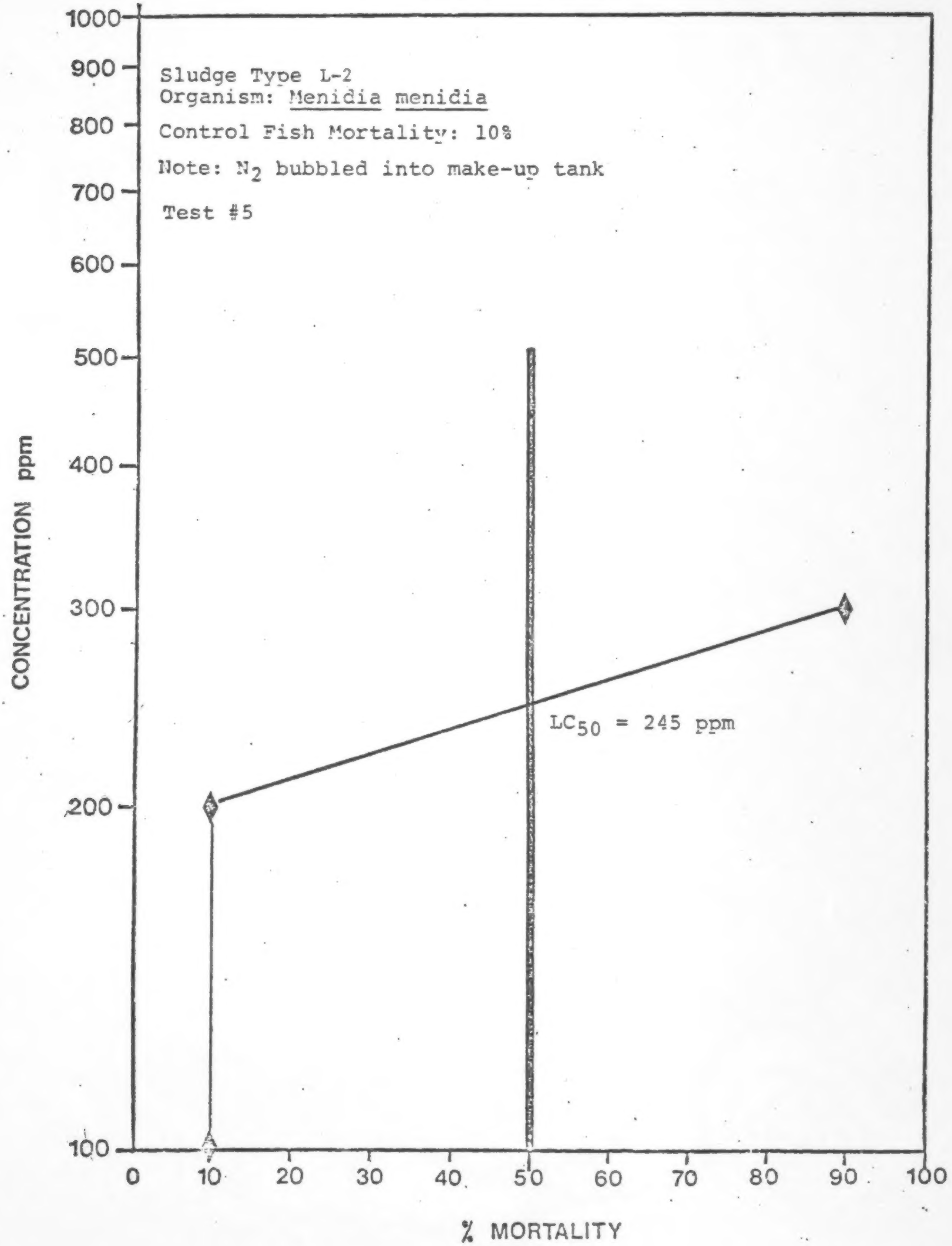
No. of Organisms: 20/test and 20/control

Test Started: 09:30 AM. Date: 11 July 1977

	Makeup Addition Time	T °C	Sal. ‰	Dissolved Oxygen, mg/1	NH_3 μgN/1	T.S.S. mg/1	$SO_3^=$ x10^6m/1	Cumul. # Dead Animals	T.O.S. mmoles/g	Ca mmoles/g	Ca/T.O.S.
Sampling Time		0.25	0.25	0.6	1.8		0.7				
Control		21.0	31.5	7.1	238		0				
A		19.5	31.5	1.0	140		1900	0	4.91		
0 Hr B		19.5	31.5	0.4	140	108	2371	0	4.59		
C		20.5	31.5	0.1	168	72	3014	0	3.88		
Sampling Time		28.0	28.0	28.0			28.3				
Control	24.0/ 27.7	21.0	31.0	7.6			0	0			
A		21.0	30.5	6.7		79	291	0			
24 Hr B		21.0	31.0	5.7		93	242	1			
C		21.0	31.0	6.8		54	457	1			
Sampling Time		49.0	49.0	49.0			49.0				
Control		21.0	31.0	7.2			0	0			
A	47.4	20.5	31.0	6.4		69	393	0			
48 Hr B		21.0	31.5	6.1		67	492	1			
C		21.2	31.0	6.1		110	566	2			
Sampling Time		71.5	71.5	71.5			72.25				
Control		20.5	31.0	7.9			0	0			
A	71.25	20.5	31.5	7.4		53	119	1			
72 Hr B		20.5	31.5	7.4		68	402	1			
C		20.5	31.0	7.5		67	597	3			
Sampling Time		99.7	95.7	95.7			95.9				
Control		21.0	31.0	7.4	189		0	0			
A		21.5	31.5	7.2	140	56	0	3	0*		
96 Hr B		21.5	31.5	7.2	98	45	0	3	0*		
C		21.5	31.0	6.9	126	46	9	5	0*		

*Below detection limit

96 HOUR BIOASSAY


Sludge Type L-2
Organism: *Menidia menidia*
Control Fish Mortality: 10%
Note: N_2 bubbled into make-up tank
Test #5

LC_{50} = 245 ppm

96 HOUR BIOASSAY

Experiment Number: 5
Sludge Type: L-2

Species: Menidia menidia
Sludge Concentration: A 100 ppm B 200 ppm C 300 ppm

No. of Organisms: 20/test and 20/control

Test Started: 16:45 AM. Date: 18 July 1977

	Makeup Addition Time	T °C	Sal. ‰	Dissolved Oxygen, mg/1	NH_3 µgN/1	T.S.S. mg/1	$SO_3^=$ x10^6m/1		Ca		Cumul. # Dead Animals
							slurry	aqueous	slurry	aqueous	
Sampling Time				0.1			0.1	0.1			0.1
Control		21.5	31.0	7.1			0	0			0
A		21.0	31.0	6.0			3476	3476			0
0 Hr B		21.0	31.0	4.7			4009	3676			0
C		21.0	31.0	3.5			9546	7678			18
Sampling Time		23.7	23.7	23.7	17.3		23.9				
Control		22.0	31.0	7.2	154		0				0
A	18.7	23.0	30.5	6.2	154		497	N.D.			1
24 Hr B		23.0	31.5	4.8	182		506				0
C		23.0	31.0	5.9	210		561				18
Sampling Time		45.0	45.0	45.0			44.6				
Control		21.5	31.5	7.0			0				1
A	43.5	22.0	31.0	6.0			676	N.D.			2
48 Hr B		22.0	31.5	5.7			488				1
C		22.0	31.0	6.[illegible]			518				18
Sampling Time		69.0	69.0	69.0			68.8				
Control		22.0	31.5	7.1			0				2
A	65.2	22.5	31.0	5.0			0	N.D.			2
72 Hr B		22.5	31.5	4.3			56				2
C		22.5	31.5	5.8			102				18
Sampling Time		90.1	90.1	90.1	90.2		89.8				
Control	89.3	22.5	32.5	7.1	224		0				2
A		23.0	32.0	5.5	182		203	N.D.			2
96 Hr B		23.0	32.0	4.8	238		249				2
C		23.0	32.0	5.9	252		425				18

Reproduced from best available copy.

Exhibit 2

Exhibit 2

96 HOUR BIOASSAY

Experiment Number: Range Finding   Species: Acartia tonsa

Number of Organisms: 10/test & 10/control   Sludge Type: L-2

Concentrations: A 100 ppm B 200 ppm C 300 ppm D 400 ppm E 500 ppm

Number of Replications: None

Test Started: 14:20 AM   DATE: 28 July 1977

		T °C	Sal ‰	Dissolved Oxygen mg/l				$SO_3^=$ x10^6 m/l slurry	$SO_3^=$ x10^6 m/l aqueous	Ca slurry	Ca aqueous	# Dead Animals
Sampling Time		0.2	0.2	0.2	0.3	0.7	1.2	0.5	0.5			
Control				7.1	7.1	7.2	7.2	0	0			0
0 Hr	A	21.5	30.5	5.6	4.2	4.9	5.9	-	-	N.D.	N.D.	0
	B			3.7	1.7	2.7	4.8	-				0
	C			2.7	1.0	2.2	4.0	111	111			7
	D			1.9	0.4	0.4	2.3	190	186			10
	E			1.8	0.2	0.4	2.1	-	-			10
Sampling Time												
Control												
24 Hr	A											
	B											
	C											
	D											
	E											
Sampling Time												
Control												
48 HR	A											
	B											
	C											
	D											
	E											
Sampling Time												
Control												
72 Hr	A											
	B											
	C											
	D											
	E											
Sampling Time												
Control												
96 Hr	A											
	B											
	C											
	D											
	E											

Reproduced from
best available copy.

96 HOUR BIOASSAY

Experiment Number: Range Finding Species: Acartia tonsa
Number of Organisms: 10/test & 10/control Sludge Type: LS-2
Concentrations: A 300 ppm B 450 ppm C 600 ppm D __________ E __________
Number of Replications: None
Test Started: 09:40 AM DATE: 29 July 1977

	T	Sal	Dissolved				$SO_3^=$ x10^6 m/1		Ca		# Dead
	°C	‰	Oxygen mg/1				slurry	aqueous	slurry	aqueous	Animals
Sampling Time	0.1	0.1	0.1	0.3	0.5	0.7	0.6	0.6			
Control			6.7	6.7	6.6	6.6	0	0			0
A			5.7	4.6	4.1	5.2	-	-			0
0 Hr B	21.0	31.0	5.3	3.7	2.3	3.8	242	204	N.D.	N.D.	0
C			4.3	2.1	0.7	2.1	262	234			10
D											
E											
Sampling Time											
Control											
A											
B											
24 Hr C											
D											
E											
Sampling Time											
Control											
A											
B											
48 HR C											
D											
E											
Sampling Time											
Control											
A											
B											
72 Hr C											
D											
E											
Sampling Time											
Control											
A											
B											
96 Hr C											
D											
E											

96 HOUR BIOASSAY

Experiment Number: 6 Species: Acartia tonsa
Number of Organisms: 15/test & 15/control Sludge Type: L-2
Concentrations: A 100 ppm B 200ppm C 300 ppm D 400 ppm E
Number of Replications: 4
Test Started: 11:50 AM Date: 1 August 1977

	T °C	Sal ‰	Dissolved Oxygen mg/l				$SO_3^=$ x10^6 m/l		Ca		Cumul. # Dead Animals
							slurry	aqueous	slurry	aqueous	
Sampling Time	0.2	0.2	0.2	0.4	1.4	2.4	0.6	0.6			
Control			6.6	6.6	6.8	7.1	0	0			8
A			6.3	5.8	6.5	7.0	28	23			0
0 Hr B			4.1	2.7	5.2	6.3	44	43			2
C	20.0	31.0	3.5	0.9	3.4	5.1	77	73			6
D			2.2	0.3	2.1	3.3	323	327			60
E											
Sampling Time			26.0	28.2							
Control			7.2	7.1							18
A			7.1	7.2							12
B	19.5	30.5	7.2	7.1							20
24 Hr C			7.2	7.2							29
D											60
E											
Sampling Time											
Control											36
A											34
B	20.0										44
48 HR C											56
D											60
E											
Sampling Time											
Control			TEST NOT COMPLETED. A.D.L. REQUESTED								
A			REVISION OF METHODOLOGY								
B											
72 Hr C											
D											
E											
Sampling Time											
Control											
A											
B											
96 Hr C											
D											
E											

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TOXICITY STUDIES:

PHASE III, OCEAN ASSESSMENT

ADL Case No. 78521-04

Progress Report #5

by

Kathleen Smith and Alice Clay
Edgerton Research Laboratory
New England Aquarium

to

Arthur D. Little, Inc.

January 10, 1978

10 Lines
to End of
Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

SECTION I: Definitive Bioassay of L2 on *Acartia tonsa*

A. PROCEDURES

Sixty young adult copepods were placed in 1-liter bottles filled with .45µ filtered seawater. Temperature, salinity, and dissolved oxygen were recorded prior to the addition of sludge. The test material was accurately weighed and added to each bottle as a solid. Food was then added at the usual rate (see Section 4 in Progress Report #4), and the bottles were filled to the top and stoppered. They were inverted every 15 minutes during the day and left upright at night. After two inversions a sulfite sample was taken and the D.O. recorded; then the bottles were refilled. Algae were added at mid-morning by removing the appropriate amount of water and adding the same amount of algal suspension. At the end of the 48-hour test period, temperature, D.O., salinity, and sulfite measurements were recorded and the copepods were counted to determine mortality.

B. RESULTS

After 48 hours a negligible number of animals had died in each of the test concentrations of 25 ppm, 50 ppm, and 100 ppm (see experiment #17). All of the animals had died within 24 hours at 150 ppm (see test 12, Progress Report #4). This mortality has a high correlation with the dissolved oxygen present, which was 2.7 at 100 ppm after 48 hours, and 0.8 at 150 ppm after 24 hours. The LC_{50} is between 100 ppm and 150 ppm (see Figure 1).

SECTION II: Definitive Bioassay of G1 on *Acartia tonsa*

The procedure used was essentially the same as that of the L2 experiment (see Section 1) except the sulfite and second D.O. measurements were not made. Concentrations of 1,000, 5,000, 10,000, and 20,000 ppm were tested. The method used for counting the copepods at the end of the experiment is discussed in Section 5 of Progress Report No. 4. The contents of the bottles were filtered through a preweighed filter, dried, and weighed to determine TSS.

Six animals died in the control bottle, 11 at 1,000 ppm, 26 at 5,000 ppm, 23 at 10,000 ppm, and 27 at 20,000 ppm (see Experiment #18). The data are illustrated in Figure 2.

After the dissolved fraction reaches saturation, the concentration stays the same regardless of loading. The test procedure does not give a good measure of suspended solid toxicity because the organisms are only subjected to the solids for the time it takes them to settle when the bottles are inverted every 15 minutes. This theory accounts for the similarity of mortalities in the higher loadings. The results are shown in Figure 3.

48 HOUR BIOASSAY

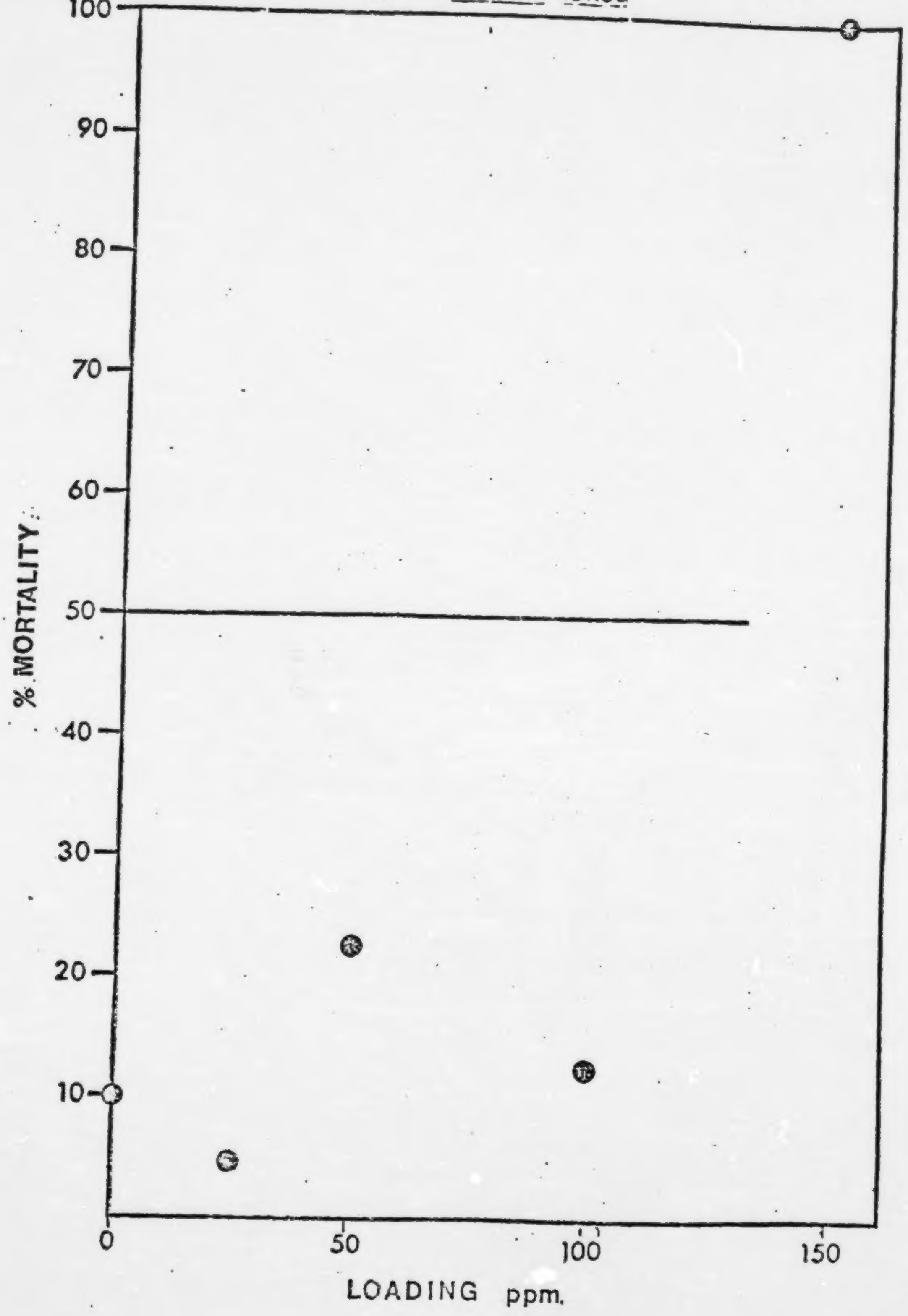
Experiment Number: 17 Species: Acartia tonsa
Number of Organisms: 60/test & control Sludge Type: L-2
Concentrations: A 25 ppm B 50 ppm C 100 ppm D______ E______
Number of Replications: 1 25 October 1977

	T °C	Sal ‰	Dissolved Oxygen mg/l			$SO_3^{=} \times 10^6$ m/l	Calcium $\times 10^4$ M/l	# Dead Animals
Sampling Time	0	0	0	.8		.8	.8	
Control	19.9	30	6.4			2.2	-	
A	19.7	30	6.4			230	1.4±1.7	
B	19.8	30	6.4			476	3.0±2.9	
0 HR C	19.8	30	6.4			582	4.9±1.1	
D								
E								
Sampling Time								
Control								
A								
B								
24 HR C								
D								
E								
Sampling Time	48	48	48			48	48	
Control	21.4	30	6.1			10	-	6
A	21.2	30	5.2			0	2.5±1.9	2
B	21.2	31	4.5			10	5.0±1.6	13
48 HR C	21.3	30	2.7			2	7.4±3.8	7
D								
E								
Sampling Time								
Control								
A								
B								
72 HR C								
D								
E								
Sampling Time								
Control								
A								
B								
96 HR C								
D								
E								

figure 1

48 HOUR BIOASSAY

L-2 - Acartia tonsa



48 HOUR BIOASSAY

Experiment Number: 18
Species: Acartia tonsa
Number of Organisms: 60/test & Control
Sludge Type: G-1
Concentrations: A 1000 ppm B 5000 ppm C 10,000 ppm D 20,000 ppm E
Number of Replications: 1
31 October 1977

		T °C	Sal ‰	Dissolved Oxygen mg/l			T.S.S. (ppm)	pH	# Dead Animals
Sampling Time		0	0	0				0	
Control		20.5	30	6.5				7.91	
	A	20.5	30						
	B	20.5	30						
0 HR	C	20.6	30						
	D	20.8	30						
	E								
Sampling Time									
Control									
	A								
	B								
24 HR	C								
	D								
	E								
Sampling Time		48	48	48			48	48	
Control		20.3	30	6.9			0	8.01	6
	A	20.4		6.8			29	7.82	11
	B	20.5		6.9			507	7.80	26
48 HR	C	20.7		7.1			4686	7.80	23
	D	20.8	32	6.7			12,725	7.80	27
	E								
Sampling Time									
Control									
	A								
	B								
72 HR	C								
	D								
	E								
Sampling Time									
Control									
	A								
	B								
96 HR	C								
	D								
	E								

Appendix B, Long-Term Exposure Testing

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Appendix B: Long-Term Exposure Testing

Excerpted from Progress Report #5 by Kathleen Smith and Alice Clay, Edgerton Research Laboratory, New England Aquarium to Arthur D. Little, Inc., January 10, 1978.

SECTION III: Long-Term Bioassay

A. EXPERIMENTAL SETUP

A photograph of the test tanks is shown on the following page. The four large tanks in the foreground will hold the flounder, and the smaller tanks will hold the *Mya*, *Littorina*, and *Zostera*. (All of the *Zostera* that were in holding at the lab have finally died, and our supplier has lost his stock. We have called as far south as North Carolina without locating any new plants.) Filtered seawater is pumped from a constant temperature bath through a manifold system into the tanks. Water flow into each tank is regulated by means of a P.V.C. needle valve. Wastewater leaves the tanks through a drainpipe at the surface.

When the system is in full operation, trace metals will be quantitatively introduced into each test tank by means of a peristaltic metering pump. The trace metal solution and the replacement water will be mixed prior to entering the tanks.

B. ADJUSTMENTS IN TANK TURNOVER RATES

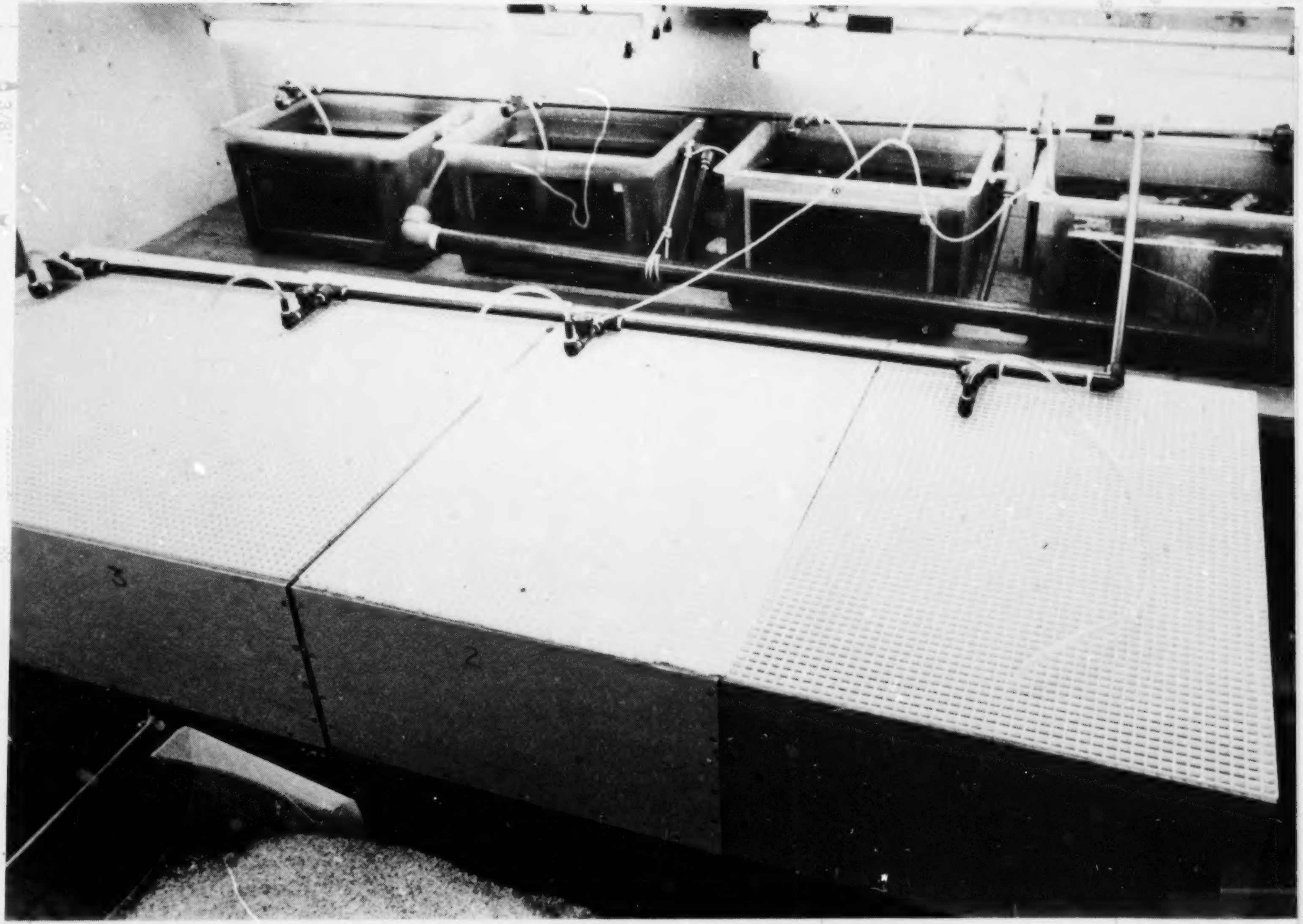
At the beginning of the experiment, when the flounder were first introduced, it was necessary to maintain a flow rate equivalent to five turnovers per day to keep the ammonia at an acceptable level of less than 500 ppb. However, after one and a half weeks it became evident that three turnovers per day would be sufficient. Two factors could account for the decrease in ammonia levels. The fish were overfed initially because they did not respond well to feeding until they became accustomed to their new environment. Secondly, the biological activity of nitrifiers on the tank surfaces may have increased with time.

10 Lines to End of Typing Area

The establishment of constant flow rates in both the flounder and *Zostera* tanks was difficult at first: they tended to decrease with time. Two manifold designs and four different pumps were tried. It was finally determined that the first pumps tried were putting out too much water, and the needle valves had to be adjusted way down to control the flow. A much smaller pump was installed which allowed the needle valves to be regulated at a more efficient portion of their range. It now appears that additional slight reductions in flow rates for the flounder tank (see Table 1) may be due to the entrapment of air at the valves. This can be alleviated by periodic manual tapping of the lines.

The *Zostera* tanks, however, are still presenting a bit of a problem. A turnover rate of two volumes daily was found to be adequate to maintain safe ammonia levels. For reasons discussed above, maintaining so slow a turnover rate has been difficult, as the data in Table 2 indicate. It may be necessary to use a higher flow rate to allow for stability. The water quality data are shown in Table 3.

B-1



Experimental Setup for Thirty-Day Exposure Test

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
TYPING GUIDE SHEET

TABLE 1

Decrease in Flow Rate Over Sixteen Hours
Tank #1 (Flounder Tank)

	Flow Rate (ℓ/min)		
Date	Initial	After 16 hrs	Change
12/13	.30	.28	-.02
12/14	.30	.25	-.05
12/15	.30	.27	-.03
12/16	.30	.28	-.02
12/19	.30	.26	-.04
12/21	.30	.26	-.04
12/22	.30	.27	-.03
12/23	.30	.27	-.03
12/28	.30	.29	-.01
12/29	.30	.30	0
Average	.30	.27	-.027

.29

Average decrease over sixteen hours
(as percentage of initial flow rate)
≈9%

TABLE 2

Decrease in Flow Rate Over Sixteen Hours
Tank #5 (Zostera Tank)

Flow Rate (ℓ/min) (Approx. 3 Turnovers/Day)

Date	Initial	After 16 hrs	Change
12/13	.16	.08	-.08
12/14	.16	.11	-.05
12/15	.16	.10	-.06
12/16	.13	.09	-.04
12/23	.15	.11	-.04
12/28	.15	.09	-.03
12/29	.15	.14	-.01
Average	.15	.10	-.04
	.12		

Average decrease over sixteen hours (as percentage of initial flow rate) ≈27%

Flow Rate (ℓ/min) (Approx. 2 Turnovers/Day)

Date	Initial	After 16 hrs	Change
12/19	.10	.02	-.08
12/20	.10	.04	-.06
12/21	.10	.03	-.07
12/22	.10	.05	-.05
Average	.10	.04	-.06
	.07		

Average decrease over sixteen hours (as percentage of initial flow rate) ≈60%

TABLE 3

Date	Tank No.	NH_3 (ppb)	D.O. (ppm)	Temperature (°C)	Salinity (ppt)
12/13	1	450	6.3	13.4	30
	5	150	8.5	14.2	30
	line	220			
12/14	1	502	5.7	13.6	30
	5	153	8.4	14.3	30
	line	196			
12/15	1	270	5.9	14.6	
	5	150	8.3	16.2	
	line	154			
12/16	1	431	6.1	14.5	30
	5	183	8.3	16.6	30
	line	166			
12/19	1	264	6.6	14.6	
	5	323	7.4	17.6	
	line	151			
12/20	1	375	6.9	13.9	30
	5	202	9.2	15.8	30
	line	205			
12/21	1	406	7.4	13.8	30
	5	212	9.6	16.1	30
	line	199			
12/22	1	392	7.6	13.4	30
	5	194	9.5	15.8	30
	line	232			
12/23	1	440	7.1	12.9	30
	5	205	10.2	13.5	30
12/27	1	230	6.5	14.6	
	5	232	7.7	14.4	
	line	163			
12/28	1	470	6.7	14.6	30
	5	205	8.5	13.1	30
12/29	1	396	6.3	12.8	
	5	250	9.2	14.6	
	line	141			

Tank #1 = Pseudopleuronectes
Tank #5 = Mya, Littorina, Zostera

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Determination of Concentrations of Metals Leached From FGD Sludges into Seawater

A leaching test of DA1, L1, and LS3 in seawater was run to determine concentrations of cadmium, zinc, nickel, selenium, and mercury leached from the FGD sludges into seawater. As agreed in a memo from Arthur D. Little, it was assumed that the three sludges contained 50% water, although this was later shown not to be the case. Percent dry weight of the three materials was: DA1, 56.8; L1, 6.9; LS3, 87.9. However, for the purpose of the leachate tests it was assumed that all solids contained 50% dry weight.

Two concentrations of sludges were used in the tests, 5% and 25%. The 5% slurries were made by mixing 100 grams of solid with 900 ml of seawater, and the 25% slurries were made by mixing 600 grams of solid with 600 ml of seawater. Thus, DA1 slurries were 5.7% and 28.4%, the L1 slurries were 6.8% and 34%, and the LS3 slurries were 8.8% and 44%. However, for convenience all slurries will be denoted as 5% and 25%.

The leachate test was run the first time using a magnetic stirrer for keeping both the 5% and the 25% slurries in suspension. However, the 25% suspension was so thick that the Teflon-coated stirring bar would become stuck in the mud that settled out. A second test was set up using Teflon mechanical stirrers for the 25% slurries maintaining a stirring rate similar to that for the 5% slurries suspended by means of magnetic stirring.

The sampling method for the second run involved pouring the well mixed FGD/seawater suspension into 50-ml polyethylene centrifuge tubes and centrifuging at 17,000 RPM for 15 minutes. The supernatants from four subsamples of each suspension were combined and poured into two other centrifuge tubes for storage. These samples were then frozen until the time of analysis.

All trace metals were measured by plasma emission spectrometry. Mercury and selenium were run using cold vapor injection systems. Zinc, cadmium, and nickel were measured by conventional nebulization of the supernatant using an automated sampling system. The results of these analyses are given in Table 1.

A problem encountered in the use of centrifugation for phase separation arose from the presence of some solid material less dense than seawater, particularly with L1. While care was taken to avoid this floating material, some inclusion of solid matter in the samples withdrawn for analysis was inevitable. A third leaching test was set up using filtration rather than centrifugation to insure the complete removal of particulate material from the test solution. Also, since their concentrations in the supernatant samples were near the analytical limits of detection, Zn, Cd, and Ni were preconcentrated using an APDC/MIBK extraction followed by back extraction with 2 M HNO_3 and 0.1 M $NaNO_3$.

TABLE 1

LEACHING TEST SECOND RUN

Concentration of Metals in Leachate (ppb)

	Cd	Zn	Ni	Se	Hg
SW	0.5±0.2	8±1		12±2	<0.2
			2 Day 5%		
DA1	3.0±5	0±9		9	↓
	0 ±4	3±7		20	
L1	7 ±2	-1±7		43	
	7 ±1	10±7		54	
LS3	10 ±5	8±9		86	
	11 ±2	15±3		71	
			2 Day 25%		
DA1				67	↓
				69	
L1				216	
				202	
LS3				150	
				166	
			4 Day 5%		
DA1	2.5±2	13±7		11	↓
	0.5±3	5±2		14	
L1	6 ±2	22±3		62	
	4 ±1	26±4		57	
LS3	11 ±2	17±3		22	
	11 ±3	17±10		90	
			4 DAY 25%		
DA1	-7 ±4	6±3		47	↓
	-3 ±6	8±1		61	
	5 ±4	17±2		321	
	7 ±3	17±3		303	
	37 ±2	27±4		157	
	42 ±4	21±3		175	

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Each of the 5% and 25% leachate samples was filtered after 2 days and 7 days in the following manner. First, the receiving flask was rinsed with 6 M HCl and then with distilled, deionized water (DDW) several times. Then, a small portion of the sample was filtered through a 0.45μ filter (cellulose acetate) into the flask and discarded. About 200-250 ml of sample (or enough solution to give $\sim$200 ml of liquid) was then filtered. A 150-ml portion was placed in a previously rinsed separatory funnel and the remaining amount saved. Another portion was filtered with 150 ml placed in a separatory funnel and the remainder saved.

Six M Ultrex HCl was added to bring the pH to 2.1. Each sample was individually tested for the amount of acid necessary. Then, 1.0 ml of 5% APDC was added, the sample shaken, and 10 ml MIBK added. The samples were shaken for one minute and allowed to stand for 7 minutes and the aqueous layer discarded. The MIBK layer was back extracted into 10 ml of a solution which was 2 M HNO_3 and 0.1 M $NaNO_3$. A spiked series of seawater samples containing 5, 10, and 15 ppb additions of Zn, Cd, and Ni were extracted each day to provide calibration standards. Additional standards were prepared directly in 2 M HNO_3 and 0.1 M $NaNO_3$. The results of the third run are listed in Table 2.

RESULTS

Mercury

Mercury was measured in the extracted and unextracted filtered leachates. All samples contained less than the detection limit of 0.4 ng. Standards of 5 and 2 ng were run for calibration purposes. The Hg found in the first leachate run was probably due to particles in the solution after centrifugation. This was noted in a later sample which was centrifuged, some of the supernatant decanted, and then the remaining centrifugate was shaken and analyzed. The decanted supernatant contained less than 0.04 ppb Hg; the suspension produced a signal too large to quantify.

Cadmium

DA1 at 5% and 25% leached out an insignificant amount of Cd over 7 days. The L1 at 5% increased the Cd concentration above the seawater level by three times over 7 days, and the 25% increased Cd levels by four times and equilibrium was reached by the second day. LS3 produced a tenfold increase in Cd at the 5% level over 7 days; the increase in Cd at the 25% level was about 30 times after 2 days and 50 times after 7 days.

Zinc

DA1 at 5% increased the Zn concentration about 1-1/2 times background over the 7-day leaching period. For the 25% level the Zn appears to be adsorbed over the 7-day period, since the concentration at the end of 7 days is about 1/5 of the background level of harbor water. In the 5% Li, Zn is only slightly increased over the 7-day period, but at the 25% loading the concentration increased to about twice the background after 7 days. The LS3 at 5% increased the Zn concentration slightly over the 7 days, but at 25% level the concentration increased to about three times the background level over 7 days.

TABLE 2

LEACHATE METAL CONCENTRATIONS (PPB) AS DETERMINED BY EXTRACTION WITH APDC/MIBK

	Cd	Zn	Ni	Se	Hg	Cd	Zn	Ni	Se	Hg
			2 DAY 5%					7 DAY 5%		
SW	0.8±0.6	10.0±0.2	1.4±0.2	7.7±3.2	<0.04					<0.04
DA1	1.6±0.9	18±1	1.1±0.3	7	↓	1.1±0.5	20±1	1.7±0.7	9	↓
	2.0±0.3	7±2	0.9±0.3	6		1.3±0.2	13±1	1.1±0.1	6	
L1	2.3±0.1	11±1	10.2±0.4	65		3.2±0.3	contam.	40±8	90	
	1.9±1.0	13±3	9.6±0.4	48		1.9±0.5	15±1	34±1	96	
LS3	6±1	10±1	2.2±0.2	66		8±1	17±1	9±1	140	
	7±1	11±1	1.2±0.1	66		8±1	10±1	8±1		
			2 DAY 25%					7 DAY 25%		
DA1	1.6±0.3	6.4±0.3	2.9±0.1	28		0.8±0.3	2±1	1.0±0.4	175	
	2.0±0.6	16±3	1.4±0.1	33		0.7±0.4	2±1	1.4±0.4	142	
L1	5±1	14±2	22±1	110		4.1±0.7	25±3	26±2	209	
	3.0±0.4	17±5	18±3	109		3.8±0.5	21±3	32±1	220	
LS3	27±2	24±2	5.7±0.4	76		42±4	30±4	10.1±0.1	202	
	25±2	19±4	7±3	97		39±3	29±3	8.1±0.3	207	
			4 DAY 5%							
DA1				14						
				16						
L1				78						
				33						
LS3				101						
				94						
			4 DAY 25%							
DA1				70						
				81						
L1				135						
				111						
LS3				106						
				114						

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Nickel

DA1 at 5% and 25% remained constant in Ni concentration over 7 days. The L1 at 5% produced an eightfold increase after 2 days and a 25-fold increase in 7 days; the L1 at 25% produced a 20-fold increase after 7 days. The LS3 at 5% gave little change in Ni concentration after 2 days but showed a sixfold increase after 7 days. The 25% leach test of LS3 showed a fourfold increase after 2 days and a sixfold increase after 7 days.

Selenium

DA1 at 5% did not leach measurable quantities of Se over 7 days, but at 25% the Se level increased to four times after 2 days, ten times after 4 days, and twenty times the background concentration after 7 days. The L1 at 5% increased to seven times at 2 days, seven times at 4 days, and twelve times at 7 days. For the 25% L1 the Se concentration increased to fourteen times at 2 days, sixteen times at 4 days, and 28 times at 7 days. The LS3 at 5% increased from eight times background at 2 days to thirteen times at 4 days, to eighteen times at 7 days. For the 25% LS3 leach test the Se concentration increased to eleven times background in 2 days, to fourteen times in 4 days, to 26 times in 7 days.

Digests

Duplicate 5-gram samples were weighed into 50-ml round-bottom flasks. Twenty-ml H_2O, 10-ml concentrated HNO_3, and 1-ml concentrated H_2SO_4 were added, and the samples were digested on a reflux column for 3 hours. After the samples cooled, 5 ml of seawater was added to each, and they were diluted to a total weight of 50 grams. The solid samples did not dissolve completely.

The samples were measured in triplicate by plasma emission spectrometry. A standard series of 0.5, 1.0, and 1.5 ppm Cd; 10, 20, and 30 ppm Ni; and 1.818, 5.636, and 5.454 ppm Zn was prepared in the same acid substrate. Hg additions of 10 and 20 ng and Se of 1 μg were used.

10 Lines to End of Typing Area

A third 5-gram sample (labeled C in Table 3) of each sludge was digested with 10-ml concentrated HNO_3 and 10-ml H_2O on a reflux column for one hour, cooled, and diluted to 100 ml. The solid sample did not dissolve completely in this case either.

The disparity of the Zn and Ni results in the digestates between the three samples of DA1 and L1, we believe, comes from the nonhomogeneity of the solid material. The DA1 solid has visible black flecks in it, and some of the material was grayer than other portions. The L1 solid also contained magnetic fine particles and was nonhomogeneous in color and consistency. Samples from all three solids were taken by scraping away about one inch of surface with a polyethylene scraper and sampling randomly the material thus exposed.

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TABLE 3

CONCENTRATIONS OF TRACE METALS IN FGD (ppm dry wt)

		Zn	Cd	Ni	Hg	Se	
DA1	A	275±14	0.30±0.04	22±1	0.541	13.2 :	
	B	0.3±0.1	0.22±0.04	8±2	0.583	15.0 :	15±1
	C	4.2±0.4	0.35±0.04	3±1		15.8 :	
L1	A	71±1	0.8±0.1	56±1	0.158	21.1 :	
	B	54±1	0.6±0.1	44±2	0.179	17.7 :	19±2
	C	51±6	0.9±0.1	32±1		19.1 :	
LS3	A	93±2	1.1±0.1	20±0.3	0.284	24.6 :	
	B	94±1	1.0±0.1	19±3	0.280	26.8 :	25±2
	C	85±5	1.3±0.2	14.5±0.2		23.5 :	

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TOXICITY STUDIES:

PHASE III, OCEAN ASSESSMENT

ADL Case No. 78521-04

Progress Report #6

by

Albert Barker,
Thomas Gilbert,
and
Kathleen Smith
Edgerton Research Laboratory
New England Aquarium

to

Arthur D. Little, Inc.

April 3, 1978

10 Lines
to End of
Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

SECTION I: Trace Metal Levels in 0.45 μ Filtered New England Aquarium Seawater

The implementation of experiment #2 (A.D. Little memorandum dated August 26, 1977) was delayed while a source of suitable, i.e., low trace metal level, seawater was found. New England Aquarium line seawater was tested first for levels of zinc, cadmium, and nickel.

A. PROCEDURE

Three liters of Aquarium line water were filtered through an acid-washed (6 N HCl) 0.45 μm Gelman-type GN-6 Metricel filter. All glassware for the filtering and extraction procedure was washed with 6 N HCl and rinsed three times with Super Q water. Three 1-liter separatory funnels each containing 800 ml of the filtered seawater were used for the extraction procedure. The pH of the water was lowered to 2.1 using 6 N HCl. A 5% solution of APDC was prepared and extracted three times using equivalent volumes of MIBK. Four ml of the APDC solution were added to each separatory funnel and mixed with the seawater. Twenty ml of MIBK were added, and the solution was shaken vigorously for 1 minute. The phases were then allowed to separate for 7 minutes. The seawater phase was drained off, and the MIBK layer was back-extracted using 5 ml of a 2 N HNO_3-0.1 M $NaNO_3$ solution. The samples were then stored in polypropylene 15-ml snap cap vials for analysis by plasma emission spectrometry. An external standard was prepared by taking 50 μl of stock standard (100 ppm Zn, 10 ppm Cd, and 20 ppm Ni) and adding it to 10 ml of 2 M HNO_3-0.1$NaNO_3$.

B. RESULTS

Aquarium line water: 0.45 μm filtered; salinity 30 ppt; pH 7.85

The values are average of three separate samples.

Metal	Concentration (ppb)
Zn	5 ± 1
Cd	0.5 ± 0.2
Ni	1.3 (based on only 2 samples)

10 Lines to End of Typing Area

SECTION II: Trace Metal Levels in "Instant Ocean" Sea Salts

A. PROCEDURE

A 5-gallon packet of "Instant Ocean" was added to 5 gallons of "Super Q" water in a 20-gallon, all glass, acid-washed aquarium. The tank was covered and the solution was stirred overnight using two Teflon stirring paddles. Three liters of water were filtered the following day through a 0.45 μ acid-washed filter. The extraction procedure was identical to that described in Section I.

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

7

B. RESULTS

Instant Ocean: Salinity 32°/oo; pH 8.59

Metal	Concentration (ppb)
Zn	>100
Ni	>100

(Analysis of the other metals of concern was halted due to the high levels of zinc and nickel.)

SECTION III: Alternative Sources of Seawater

The collection of seawater from Massachusetts Bay was considered. However, trace metal data collected at a site 40 km off Boston showed levels of the metals of concern no lower than those from the filtered aquarium water. Another possibility was to pretreat the seawater with "Chelex 100," a chelating ion exchange resin which has a high preference for many of the transition elements. Unfortunately, the resin has a very low affinity for selenium and a somewhat higher preference for calcium and magnesium.

SECTION IV: Quiescent Leaching Rate Experiments

A. PROCEDURES

The experimental procedure followed the guidelines given in an A.D. Little memo dated January 17, 1978. Six 20-gallon fiberglass aquariums measuring approximately 53 cm long x 38 cm wide x 36 cm high were used for the tests. All the tanks were washed with 6 N HCl prior to the introduction of the sludge. The sludge was added to the tanks according to the specifications in Table 1.

10 Lines to End of Typing Area

Table 1

Initial Sludge and Water Depths

Tank #	Experiment #	Material	Sludge Layer (cm)	Seawater Layer (cm)
1	A	DA1	7.5	7.5
2	B	L1	7.5	7.5
3	C	LS3	7.5	7.5
4	D	LS3	2.5	23
5	E	LS3	15	15
6	Control	---	---	30

For Page Numbering

DL 054 1/79 300M

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Filtered seawater was carefully added to each tank to minimize suspension of the sludge layer. Even with this precaution, some fines were suspended in the tanks; however, they settled out within one hour. After the addition of the water the sludge depths were somewhat lower due to settling and compaction. The final depth values are listed in Table 2.

Table 2

Final Sludge Depths

Experiment #	Sludge	Depth (cm)
A	DA1	6.3
B	L1	6.8
C	LS3	5.8
D	LS3	1.5
E	LS3	13

All the tanks were covered with polyethylene film to prevent airborne contamination. A 30-RPM motor with a glass stirring rod was mounted above each tank (see Figure 1) to provide mixing of the seawater without resuspending the sludge layer. The tanks with the two sulfite-rich sludges, DA1 and L1, had nitrogen flowing into the air layer above the water to reduce the oxidation rate.

At each sampling time prescribed by the A.D. Little memo of January 17, 1978, 1 liter of seawater was taken from each tank and filtered through a 0.45 μm filter. Initial pH values were recorded for the first few sampling dates to determine the amount of acid needed in the extraction procedure. The samples were then extracted using the same procedure described in Section I; and levels of zinc, cadmium, and nickel were determined by plasma emission spectrometry (PES). Standards were prepared by adding the stock solution described above to filtered line water samples. The increases in metal concentrations were 25 ppb Zn, 2.5 ppb Cd, and 5.0 ppb Ni. Extracts of these samples and of unspiked line water provided two point-calibration curves for PES measurements. For selenium, samples were taken from the test tanks and analyzed directly using a hydride generation technique and PES (at the request of Arthur D. Little staff, mercury measurements were excluded because prior data taken in the maximum concentration tests showed mercury levels for all sludges was below the detection limit of 0.04 ppb). Temperature and dissolved oxygen data for each tank is given in Exhibit 1, while sampling time and pH values are given in Exhibit 2.

10 Lines to End of Typing Area

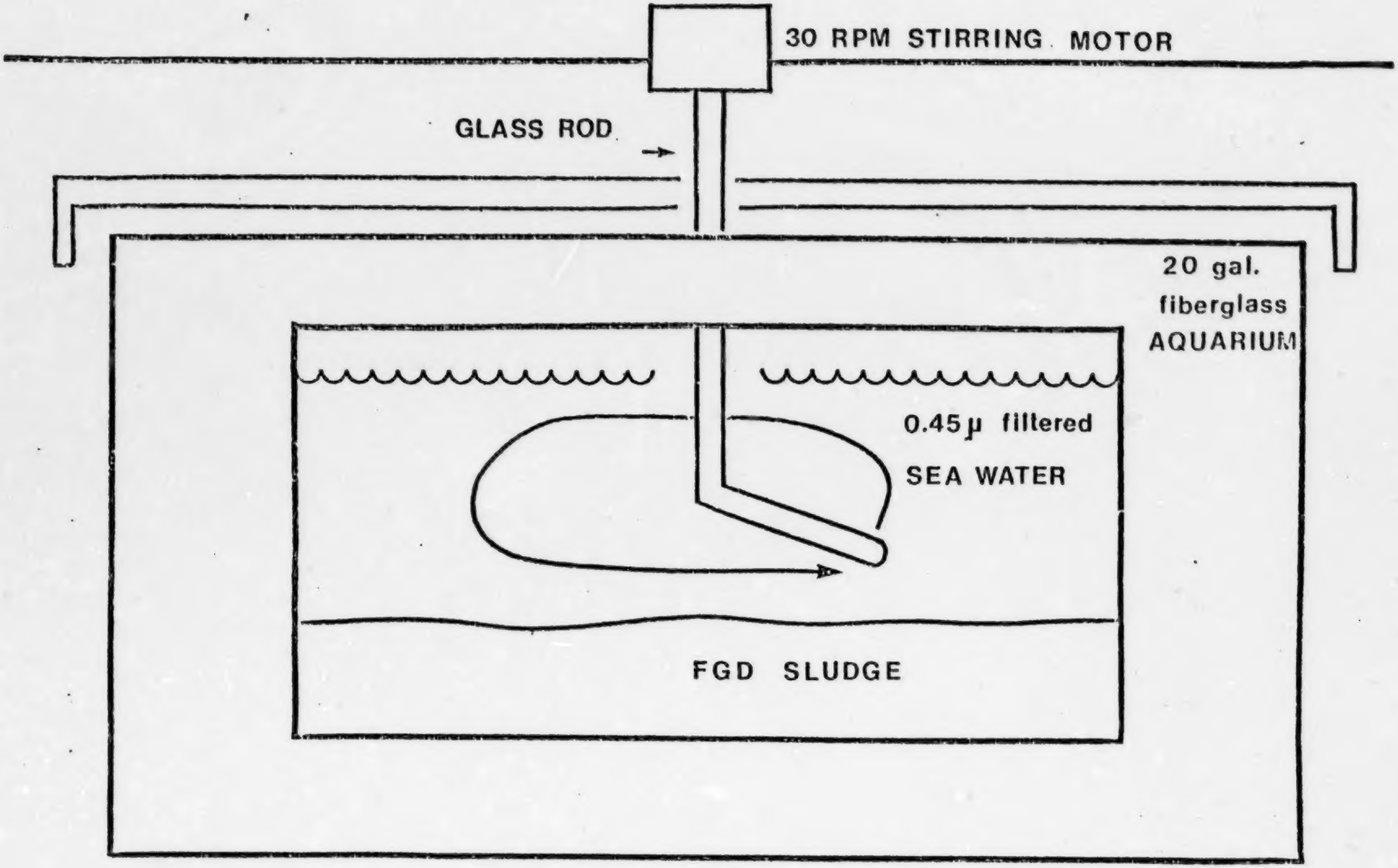
B. RESULTS

1. Observations During APDC/MIBK Extractions

Following acidification of the seawater subsamples and the addition of APDC, the samples sometimes turned a pale pink. This color was observed

For Page Numbering

FIGURE 1


30 RPM STIRRING MOTOR
GLASS ROD
20 gal.
fiberglass
AQUARIUM
0.45µ filtered
SEA WATER
FGD SLUDGE

CENTER OF PAGE
TOP OF IMAGE AREA

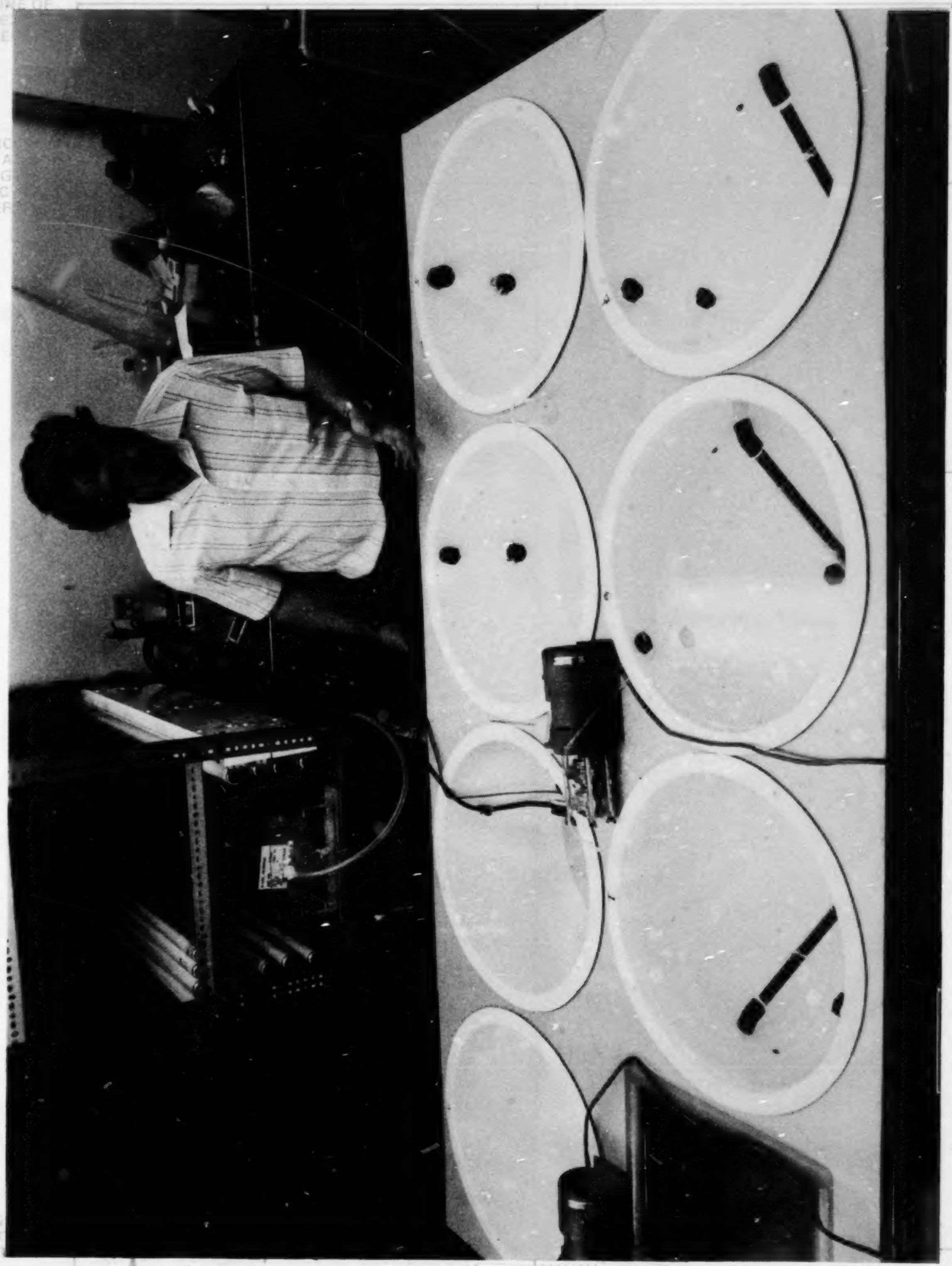


Figure 2 Menidia Bioassay Setup

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8''
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
© U.S. GOVERNMENT PRINTING OFFICE 1981-560-058
TYPING GUIDE SHEET

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

initially only in samples taken from the tank containing L1 sludge. Samples taken after longer exposure intervals produced more intense pink color for L1 samples and later for LS3 samples. After these samples had been extracted with MIBK and the aqueous layer had been drained, pink precipitates were observed on the separatory funnel walls. The MIBK extracts of all four FGC leachates were a yellowish-brown color, indicating unusually high levels of dissolved organic matter. The color was not bleached by the back extraction of metal-PCD complexes with the 2 $\underline{N}$ NHO_3-0.1 $\underline{M}$ $NaNO_3$ solution; however, the pink precipitate was dissolved.

2. Results of Trace Element Measurements

The results of Cd, Zn, Ni, and Se measurements are presented in Table 3 and in Figures 2 to 4. The cadmium data produced the most easily discernible trends. Dissolved Cd concentrations in the control tank and in Tank #2 containing DA1 showed no significant changes with time. However, Cd levels rose, quickly at first, in all the L1 and LS3 leachates and appeared to have approached equilibrium levels after two weeks. Among the LS3 leachates the greatest dissolved Cd concentrations were found in Tank #3, the next highest were in Tank #5, and with the exception of the samples taken on March 8 the lowest Cd concentrations occurred in Tank #4. This trend is an inverse function of the depth of the seawater in each of the three tanks and could be taken to mean that there is a limited supply of leachable Cd in the quiescent FGC substrates, perhaps released only from these surface layers.

Interpreting the Zn data is more difficult. In addition to a lot of scatter in the results for individual tanks, dissolved Zn levels in the control tank often exceeded those in the tests. In most tanks, Zn levels reached a maximum after several days and then declined toward the end of the exposure period. The mechanism behind this behavior is not clear. It may be that the major source of Zn in the tanks is not FGD sludge but rather the tanks themselves. This would explain the increase in Zn in the control tank but not necessarily the decrease in Zn toward the end of the test period. One trend is clear: seawater in contact with DA1 sludge consistently contained Zn concentrations below those of water over the L1/LS3 sludges and also below that in the control tank. Possibly, the layer of DA1 inhibited the desorption of Zn from the bottom surface of the tank, although that mechanism alone would not explain Zn levels much lower than in the L1/LS3 tanks. The depressed levels may mean that DA1 is, in fact, an effective adsorber of Zn from seawater. Its adsorptive properties were likely enhanced by the alkalinity it imparted to the overlying seawater. The presence of the L1/LS3 sludges results in a slight, and not accurately quantified, increase in dissolved Zn concentrations.

10 Lines to End of Typing Area

The nickel data offer little informational value with the exception that L1 released significant amounts after 14 days. The leaching of Ni may have happened sooner, but the scatter in the data make such a conclusion tentative at best. The reason for the scatter in the Ni data from the first week of testing may be the elevated levels of dissolved organic

For Page Numbering

TABLE 3

HEAVY METALS IN SEAWATER OVERLYING FGD LAYERS
(Concentrations in ppb)

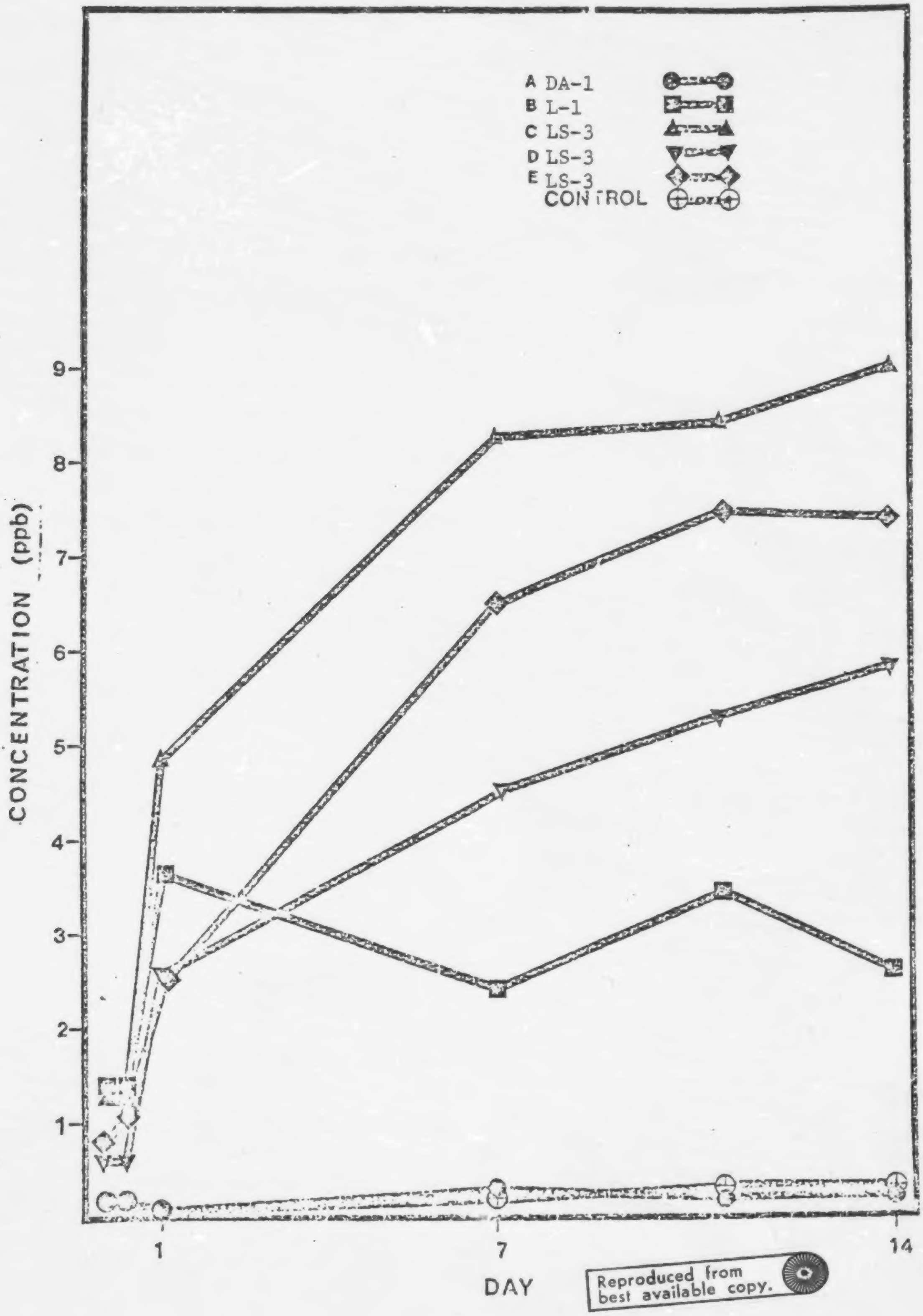
Material/% By Volume	DA-1; 50%	L-1; 50%	LS-3; 50%	LS-3; 50%	LS-3; 50%	Control
TANK No.	1	2	3	4	5	6
	●—●	■—□	▲—▲	▼—▼	◆—◆	⊖—⊖
CADMIUM Leaching Period						
4 hr	0.2	1.4	1.3	0.6	0.8	0.2
6.5 hr	0.2	1.4	1.2	0.6	1.0	0.2
24 hr	<0.1	3.6	4.9	2.6	2.5	<0.1
7 days	0.3	2.4	8.3	4.5	6.5	0.2
11 days	0.2	3.4	8.4	5.3	7.5	0.3
14 days	0.2	2.6	9.0	5.8	7.4	0.3
31 days	0.3	4.1	26.0	8.6	18.0	0.3
ZINC						
4 hr	3	17	14	11	15	5
6.5 hr	4		14	14	18	10
24 hr	11	14	57	19	21	20
7 days	1	10	27	18	20	21
11 days	2	6	13	15	20	21
14 days	3	7	16	14	32	18
31 days*	9±1	19±2	35±8	14±8	12±4	8 5±7 (n=4)
NICKEL						
4 hr	2	16	7	6	10	4
6.5 hr	6	48	5	6	7	4
24 hr	65	20	5	65	5	<5
7 days	4	15	5	4	14	8
15 days*	<7	42	8	7	10	<7
31 days*	8±5	25±6	28±5	10±5	18±4	0±7 (n=3)
SELENIUM						
4 days	3,4	219	19	16,13	15	3
9 days	2	132	35	17	19	6,3
11 days	2	210	39	27	46	3
14 days	8	104	56	19	26	3
31 days	6	100	64	33	54	5

*non-extracted samples

Ni data for day 15 were from non-filtered samples

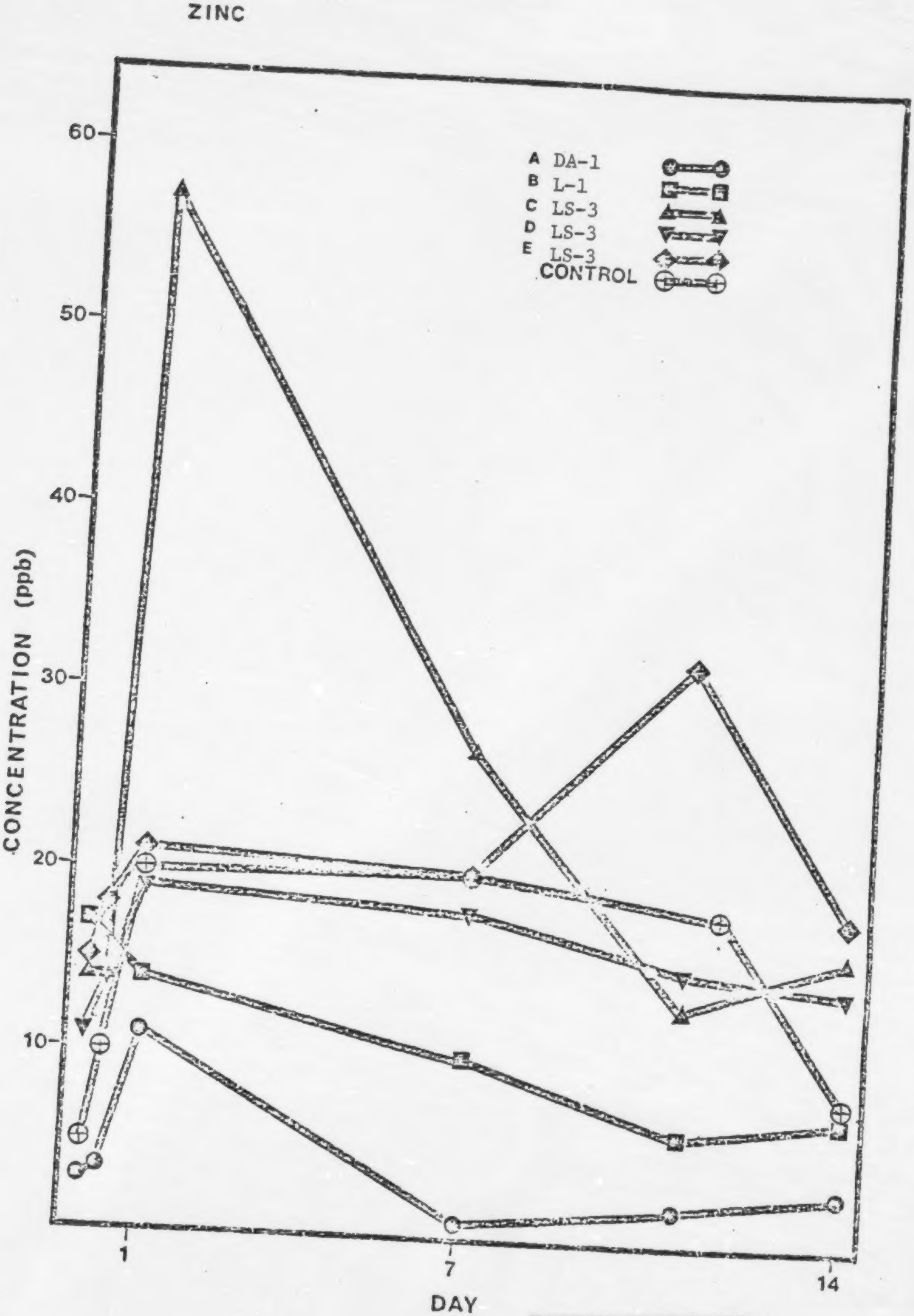
FIGURE 3

CADMIUM



Reproduced from best available copy.

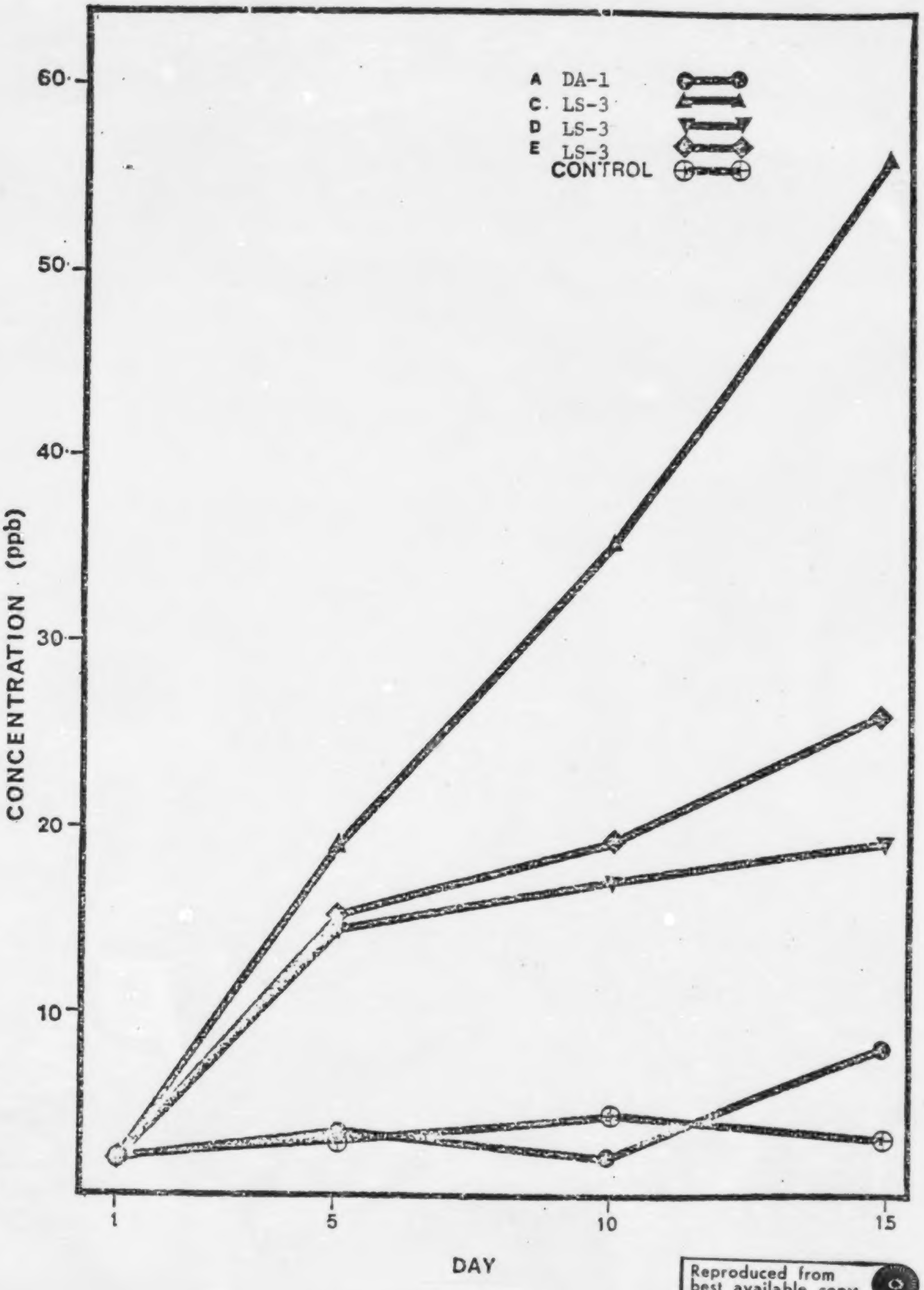
FIGURE 4



Reproduced from best available copy.

FIGURE 5

SELENIUM



Reproduced from best available copy.

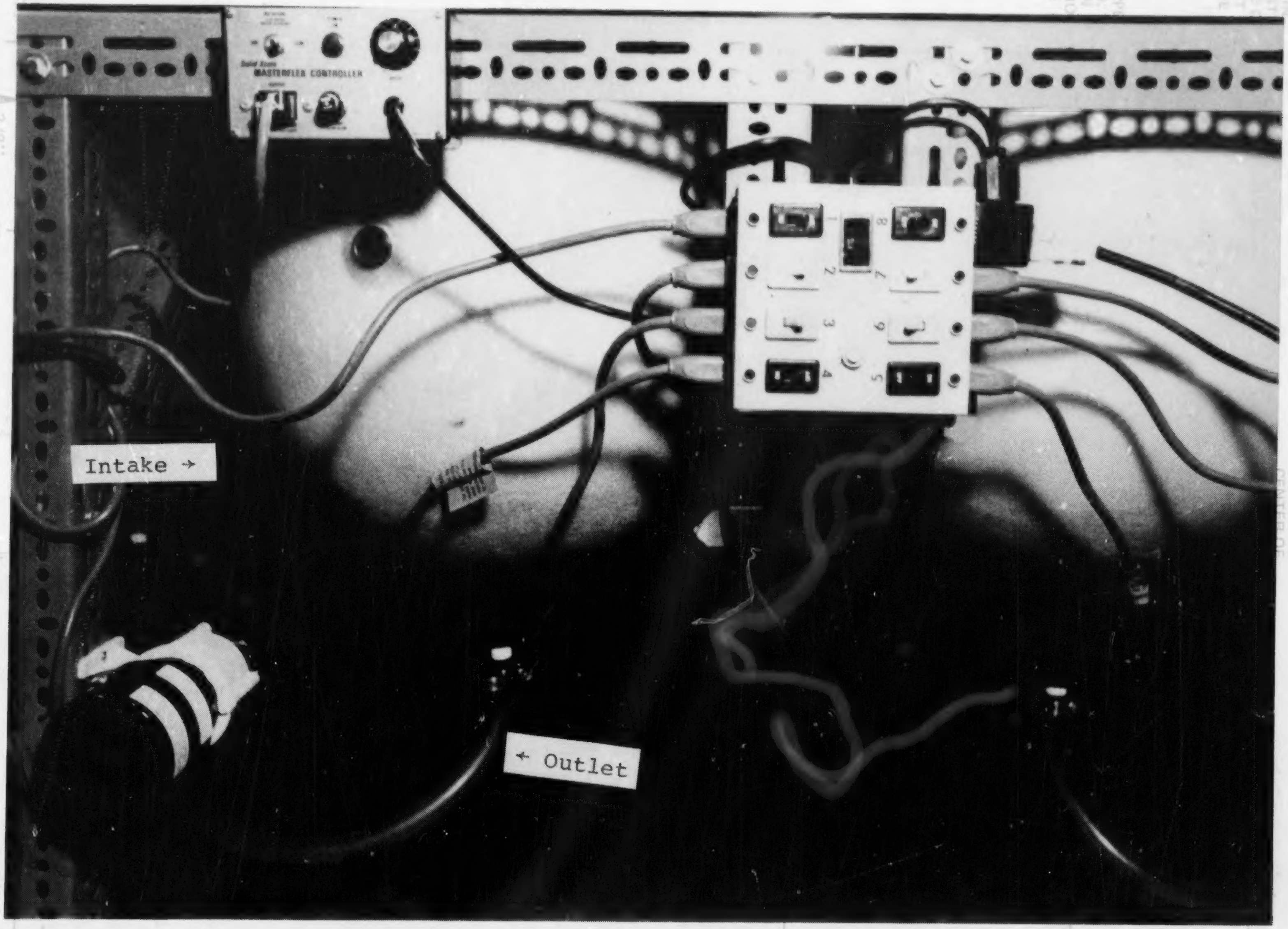

MASTERFLEX CONTROLLER
1
2
3
4
5
6
7
8
Intake →
← Outlet

Figure 6. Suspension Pump for Menidia Bioassay

Reproduced from
best available copy.

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
TYPING GUIDE SHEET

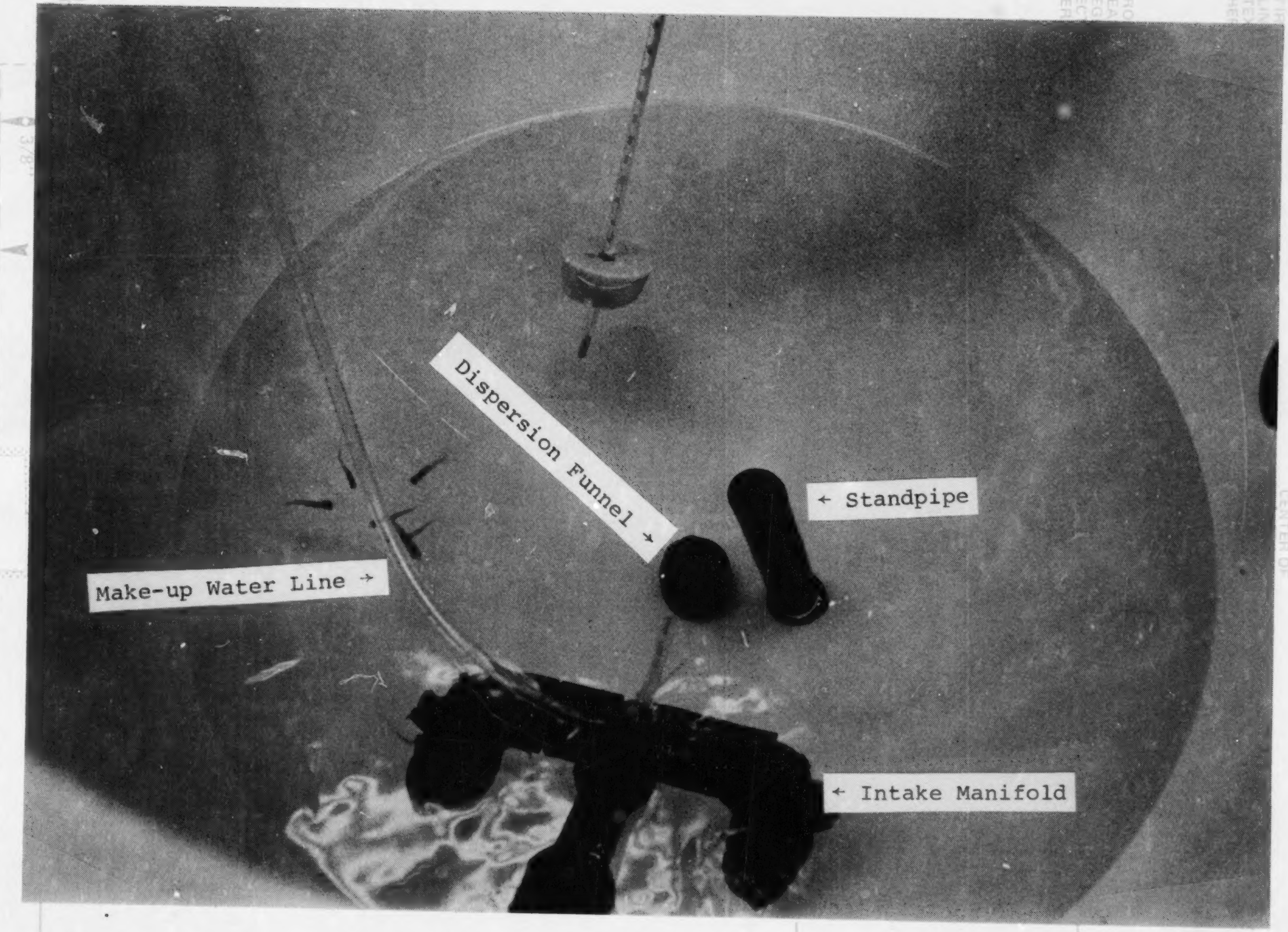

Dispersion Funnel →
← Standpipe
Make-up Water Line →
← Intake Manifold

Figure 7. Menidia Bioassay Tank

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
U.S. GOVERNMENT PRINTING OFFICE
TYPING GUIDE SHEET

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

matter in the sludge leachates. In an evaluation of the APCD/MIBK extraction system for trace metal analyses in seawater, Stolzberg* found that the extraction of Ni was inhibited by the presence of other organic chelators, particularly EDTA. The extraction of zinc was also inhibited but to a lesser extent, and the extraction of Cd was not noticeably affected. It is notable that the likely degree of extraction inhibition among the three elements is Ni>Zn>Cd, or the inverse of the relative precision with which these metals were measured in the FGD leachates.

The Ni data for 15 days of leaching were acquired by the direct nebulization of the seawater samples into the plasma spectrometer. While 5 of the 6 samples were at or below the limit of detection of 7 ppb, the Ni concentration in the leachate from the tank containing L1 was 42 ± 9 (n = 3) ppb. If these tests are to be extended, the direct measurement of both Ni and Zn (limit of detection = 3 ppb) would be more desirable than continued preconcentration with APCD/MIBK.

The results of selenium measurements show that there was no significant release of this element from DA1. Leachate from this sludge contained Se levels that closely resembled those of the control tank. The leaching of Se from the LS3 substrates followed the trend observed for Cd: the highest concentrations occurred in Tank No. 3, the lowest were found in Tank No. 4, and intermediate levels were observed in Tank No. 5. Leachate samples from L1 contained the highest and most variable Se concentrations. The variation appeared to be a function of sample handling. Those taken from the tank and analyzed immediately contained relatively high Se levels, as did those samples that were frozen soon after sampling, then quickly thawed and analyzed. However, those samples allowed to thaw overnight and analyzed the following day contained lower Se levels. Analyses of samples treated in this way produced the data shown in Figure 4. To evaluate the effect of freezing and thawing, samples taken from Tank No. 2 on March 10, 15, and 17 were analyzed, then refrozen, thawed, and analyzed again. The samples had lost 43, 42, and 56% of the Se content measured initially. We recommend that any future Se measurements be made immediately after the samples are taken.

10 Lines to End of Typing Area

---

* Stolzberg, Richard Jay. "Ammonium pyrrolidine carbodithioate-Methyl Isobutyl Ketone Extraction System for Some Trace Metals in Seawater." Analytical Methods in Oceanography, American Chemical Society, Washington, D.C. 1975.

For Page Numbering

054-1279 200M

EXHIBIT 1

Tank #	Sludge	Date	Temp. (°C)	D.O. (ppm)	NOTES
1	DA1	10 March	18.0	4.2	
		13 March	18.5	4.1	
		14 March	18.0	3.2	
		15 March	18.0	2.7	
		16 March	17.9	3.2	
		17 March	18.0	4.3	
		20 March	18.8	4.3	
		21 March	17.2	7.5	N_2 ran out during night
		22 March	17.5	5.2	
		23 March	17.9	4.3	
		24 March	18.3	1.6	
		27 March	15.4	3.3	
		29 March	18.3	3.0	
2	L1	10 March	18.5	0.7	
		13 March	18.5	0.3	
		14 March	18.0	0.3	
		15 March	18.0	0.2	
		16 March	18.3	0.4	
		17 March	18.0	0.3	
		20 March	19.4	0.4	
		21 March	17.6	1.4	N_2 ran out during night
		22 March	18.0	0.5	
		23 March	18.2	0.5	
		24 March	18.8	0.9	
		27 March	15.9	1.4	
		29 March	18.7	0.7	
3	LS3	10 March	18.5	7.4	
		13 March	19.0	7.2	
		14 March	18.5	7.0	
		15 March	18.5	7.1	
		16 March	18.7	7.7	
		17 March	18.2	7.3	
		20 March	19.8	7.2	
		21 March	18.0	7.4	
		22 March	18.2	7.4	
		23 March	18.6	7.4	
		24 March	19.0	7.4	
		27 March	15.9	8.1	
		29 March	18.9	7.4	

EXHIBIT 1
(Continued)

Tank #	Sludge	Date	Temp. (°C.)	D.O. (ppm)	NOTES
4	LS1	10 March	19.0	7.6	
		13	19.0	7.2	
		14	18.5	7.0	
		15	18.5	7.1	
		16	18.9	7.6	
		17	18.5	7.4	
		20	19.9	7.2	
		21	18.6	7.5	
		22	18.5	7.4	
		23	18.8	7.4	
		24	19.1	7.4	
		27	16.1	8.0	
		29	18.9	7.4	
5	LS1	10 March	19.0	7.5	
		13	19.0	7.1	
		14	18.5	7.0	
		15	19.0	7.1	
		16	18.9	7.7	
		17	18.5	7.4	
		20	19.8	7.1	
		21	18.5	7.5	
		22	18.7	7.5	
		23	18.9	7.3	
		24	19.2	7.5	
		27	16.2	8.1	
		29	19.0	7.5	
6	Control	10 March	18.0	8.0	
		13	18.5	8.0	
		14	18.0	7.1	
		15	18.0	7.1	
		16	18.3	7.6	
		17	18.0	7.5	
		20	19.0	7.4	
		21	17.1	7.5	
		22	17.8	7.7	
		23	17.7	7.7	
		24	18.0	7.7	
		27	15.3	8.2	
		29	18.3	7.6	

EXHIBIT 2

Date	Exp. #	Tank #	Sludge	Sample Time	pH
6 March	A	1	DA1	15:10	9.15
	B	2	L1	15:30	8.58
	C	3	LS3	15:55	7.57
	D	4	LS3	16:10	7.81
	E	5	LS3	16:25	7.75
	-	6	Control	16:40	7.51
6 March	A	1	DA1	17:45	8.94
	B	2	L1	18:00	-
	C	3	LS3	18:10	-
	D	4	LS3	18:20	-
	E	5	LS3	18:30	-
	-	6	Control	18:40	-
7 March	-	-	Linewater	-	8.01
8 March	A	1	DA1	15:50	9.93
	B	2	L1	15:40	8.61
	C	3	LS3	15:10	-
	D	4	LS3	14:50	-
	E	5	LS3	14:40	-
	-	6	Control	14:30	-
	-	-	Linewater	-	7.94
10 March	A	1	DA1	14:30	9.73
12 March	A	1	DA1	11:30	9.82
	B	2	L1	16:10	8.66
	C	3	LS3	16:00	8.06
	D	4	LS3	15:20	7.89
	E	5	LS3	15:00	7.97
	-	6	Control	14:30	7.64
	-	-	Linewater	13:00	8.02
	-	6	Control	11:00	8.16
17 March	A	1	DA1	15:10	
	B	2	L1	15:00	
	C	3	LS3	14:25	
	D	4	LS3	14:00	
	E	5	LS3	13:30	
	-	6	Control	13:00	
	-	-	Linewater	15:50	
20 March	A	1	DA1	15:05	
	B	2	L1	14:45	
	C	3	LS3	14:25	
	D	4	LS3	14:10	
	E	5	LS3	13:45	
	-	6	Control	13:30	
	-	-	Linewater	15:20	
	-	-	Linewater	15:25	
	-	-	Linewater	15:50	
	-	-	Linewater	15:55	

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

TOXICITY STUDIES:

PHASE III, OCEAN ASSESSMENT

ADL Case No. 78521-04

Progress Report #7

by

Albert Barker,
Kathleen Smith

to

Arthur D. Little, Inc.

August 15, 1978

10 Lines
to End of
Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Long-Term Bioaccumulation Tests

Experimental Setup

The original tanks and equipment described in Section III of Progress Report #5 were used for the tests, with only a few minor modifications. Flow meters were installed on all incoming tank lines to allow for more accurate control of the turnover water. Turnover rates were increased to four times a day for the flounder tanks and 5 times a day for the eelgrass tanks to obtain more consistent flow over the long testing period. (Flow rates have been maintained within 90% of theoretical during the test thus far.) The trace metal stock solutions were metered into the L1 and LS3 tanks by a peristaltic pump (see photograph of entire setup on following page). The following table gives tank and sludge makeup:

Tank No.	Organism	Sludge Type	Sludge, %
1	Flounder	Control (sand)	---
2	Flounder	L1	16" sq.
3	Flounder	LS3	25%
4	Flounder	DA1	16" sq.
5	Clam, periwinkle, eelgrass	DA1	50%
6	Clam, periwinkle, eelgrass	LS3	50%
7	Clam, periwinkle, eelgrass	L1	50%
8	Clam, periwinkle eelgrass	Control (sand)	

Preliminary Test Using Flounder and DA1

10 Lines to End of Typing Area

One-quarter of the bottom of the tank, approximately 80 sq.in., was covered with a 1" depth of DA1; and three-quarters, with gravel. DA1 was chosen because of its high sulfite content. Five flounder (Pseudopleuronectes americana) were placed in the tank; four swam to the sand and one to the DA1. Initially, all of the fish were respiring a little fast due to the handling stress. All of the flounder except the one on the sludge "dug in" soon after being transferred. After approximately 10 minutes the fish on the DA1 had turned around and was lying with its anterior end at the gravel-sludge interface. After an additional 10 minutes it had moved forward so that only its posterior half was on the sludge and it had begun to "dig in." Six hours later none of the fish had moved significantly. By 8 a.m. the following day all the fish were dead, one having jumped out of the tank. The D.O. had dropped to 2.4 ppm from the 6.3 ppm of the previous afternoon. The ammonia was 126 ppb. Much of the DA1 was spread throughout the tank and covered the gravel.

BEGIN FIRST LINE OF TEXT HERE
DROPPED HEAD; BEGIN SECTIONS HERE
CENTER OF PAGE
TOP OF IMAGE AREA

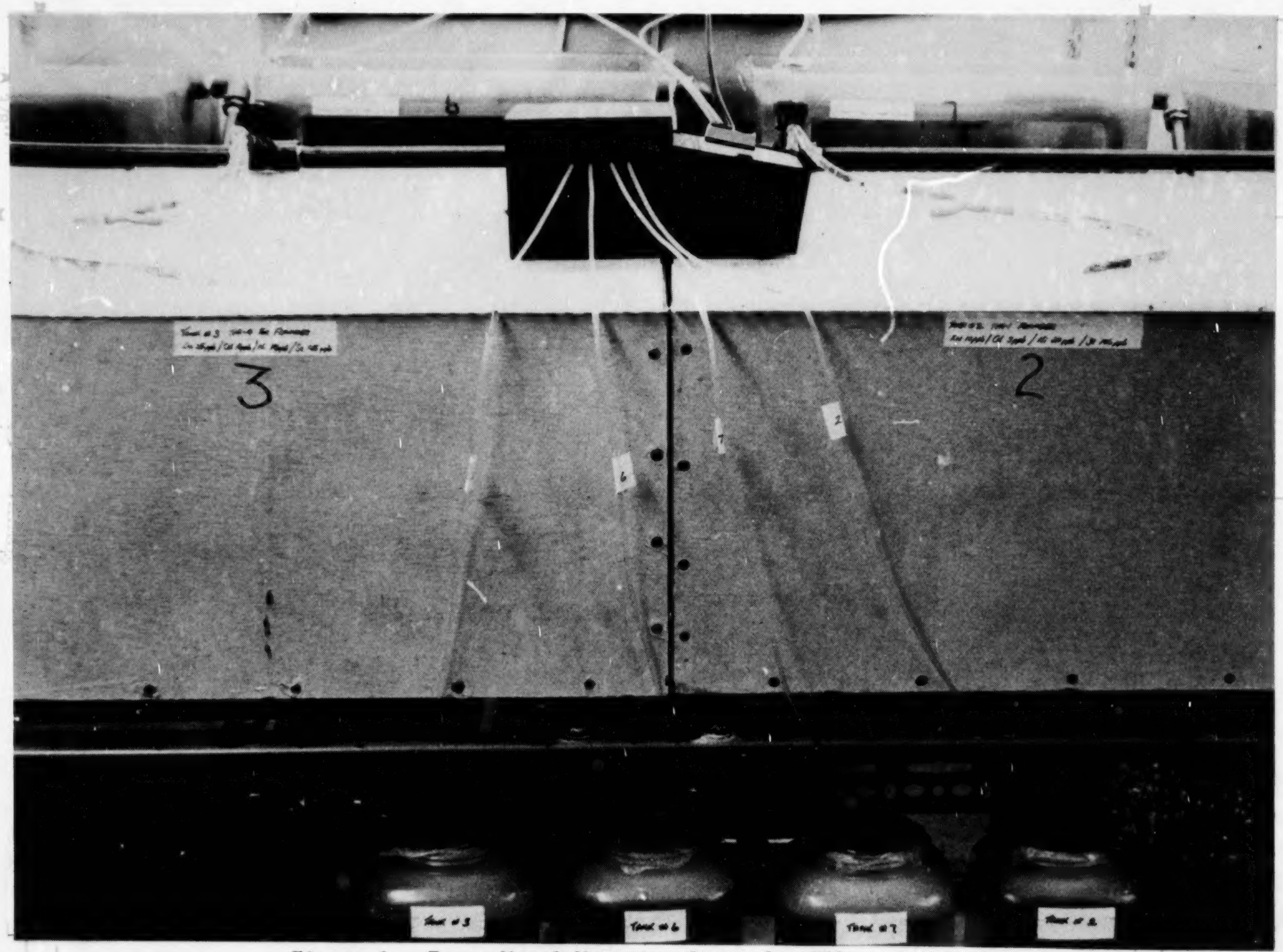


Figure 1. Trace Metal Metering Setup for Thirty-Day Tests

Reproduced from best available copy.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
U.S. GOVERNMENT PRINTING OFFICE
TYPING GUIDE SHEET

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

The experiment was then repeated with a small patch of DA1 in one corner of the tank, approximately 16 sq.in. The flounder were very active when first placed in the tank. Three of the five fish settled down with their anteriormost part directly on the DA1. By 8:30 the following morning one fish had died and one other was in very bad condition. The D.O. had fallen to 1.3 from 7.7. The flow rate was increased slightly to improve the D.O. situation and the four remaining fish did recover somewhat. Two of them swam up the walls of the tank periodically, one in the area of the DA1 patch. By the end of the day the fish had calmed down considerably but would not eat and were still respiring heavily. The D.O. continued to fluctuate and the fish were respiring very fast; the flow was increased to approximately five tank turnovers per day. At 3 p.m. another flounder had died. The following morning the three remaining fish were quiet; the D.O. was 5.6 and remained stable over the weekend. About one-half of the DA1 had been mixed with the gravel throughout the tank.

From these two tests it was obvious that only a small amount of the sulfite-rich sludges could be used in the flounder test tanks.

Preliminary Test Using Eelgrass, Softshell Clam, Periwinkle, and DA1

One-half of the bottom of the tank was covered with a 3" layer of DA1, and the remaining half with fine gravel. Three Mya and three Littorina specimens were placed on the sludge, and three of the others on the gravel. The Zostera were left in the soil they were growing in, and the whole bed was placed in the tank so that one-half the bed was surrounded by DA1 and one-half by gravel.

In the first 15 minutes one Littorina had moved onto the sludge. Within 1-1/2 hours one of the Littorina from the DA1 side had gotten on top of a Mya and one other had left the sludge area. One Littorina was having much difficulty getting a foothold on the DA1 and remained upside-down overnight; it was making some progress toward the wall of the tank.

10 Lines to End of Typing Area

By the end of the first day the D.O. had dropped from 7.0 to 6.5 ppm. The following morning the D.O. was 4 ppm. After the weekend the D.O. was 5.1, and there were no Littorina near the DA1 except one still on a Mya and one on the wall above. The next morning the D.O. was 2.8; after readjustment of the flow rate the D.O. increased to 4.6. The following day two Mya were found dead. The flow rate had not dropped appreciably overnight, but during the night the D.O. fell to 2.7 ppm. By this time, DA1 could be seen covering much of the gravel. This appeared to have been caused by the exhalent current from the Mya. The flow rate was maintained at five turnovers per day from this point on. The position of the animals and D.O. remained stable for the duration of the test (5 days).

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8 1/2 x 11

TOP

Trace Metal Additions

Stock solutions were made up from $ZnCl_2$, $NiCl_2$, $CdCl_2$, and H_2SeO_3 to be about 1.0% of the metal. These solutions were calibrated against standards on the plasma:

Cd, Zn = 1.00%
Ni, Se = 0.94%

A second solution of selenium was needed at the end of July:

Se = 0.98%

Mixed L1 and LS3 stock solutions were made combining the 1% stocks in volume ratios to give the following elemental ratios:

	Zn	Cd	Ni	Se
L1	10	4	20	106
LS3	25	18	18	95

These mixed stock solutions were then diluted as needed with 0.45μ filtered Boston Harbor water so that when pumped at 1/ml/minute into the test tanks, the concentrations of metals were as indicated (ppb above background).

	L1	LS3
Zn	10	25
Cd	4	18
Ni	20	18
Se	106	95

Since the water flow rate into the flounder tanks was initially 320 ml/minute, the concentrations of the elements in the diluted flounder tank stocks were 320 x the above values:

10 Lines to End of Typing Area

18.9 ml L1 stock/4ℓ seawater
20.9 ml LS3 stock/4ℓ seawater

Since water flow into the *Zostera* tanks was 140 ml/minute, the following dilutions were made:

8.3 ml L1 stock/4ℓ seawater
9.1 ml LS3 stock/4ℓ seawater

On July 7, the flow rates in *Zostera* tanks were changed to 230 ml/minute. Therefore, 13.6 ml of L1 or 15.0 ml of LS3 was diluted with 4ℓ of seawater.

33 For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

On August 2, a new L1 mixed stock made up with 0.98% Se was added at these rates:

18.4 ml/4ℓ in the flounder tank
13.2 ml/4ℓ in the *Zostera* tank

The metal-seawater solutions are pumped into the test tanks from 4-liter containers. After 48 hours, about one liter is left in the container and three liters are made up and added.

Sampling

1) Schedule: July 3, 5, 7, 14, 18, 21, 28
   August 2, 10, 17
   10 a.m.

2) Water Samples:

   a) Collected by dipping a beaker into the tank (beaker was initially acid-soaked and rinsed; during the experiment it was kept covered with aluminum foil).

   b) 800 ml from each tank were measured into 1-liter polyethylene bottles. Samples scheduled to be analyzed were done that day by APDC extraction for Ni, Zn, and Cd; those to be stored were frozen.

   c) 100-125 ml were put into 150-ml disposable flasks (originals and duplicates) and frozen for later Se analysis.

3) Organisms:

   a) The flounder from the large tanks and the *Mya*, *Littorina*, and *Zostera* from the small tank subjected to the same conditions were collected in the same beaker and stored in the same polyethylene bag.

   b) The original set was taken from the gravel side of the tank; the duplicates, from the sludge side.

   c) The flounder were caught in a fish net; the others were picked out by hand. When possible, the *Littorina* were taken from the bottom. Roots from the *Zostera* were taken as part of the plant.

   d) Samples were rinsed in Super-Q, put in plastic bags, and frozen until analyzed.

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Water Analysis

Zinc, cadmium, and nickel are analyzed by APDC/MIBK extraction procedures (ammonium pyrrolidine carbodithioate-methyl isobutyl ketone). Extractions starting July 18 have been done with a PDCA (the acid form of APDC)-$CHCl_3$ system. The PDCA was synthesized from redistilled pyrrolidine and carbon disulfide. (This procedure was adopted because of contamination in the APDC). A 6-point calibration curve is obtained from the extracts of three spiked and three unspiked 800-ml portions of filtered seawater. Procedural blanks and external standards are prepared by adding the appropriate volumes of reagents to Pyrex beakers, taking the mixture to dryness, and then digestion with nitric acid.

All glassware used is acid soaked (1:160 HNO_3) overnight and rinsed with Super-Q water; when not in use, it was kept covered with Parafilm.

APDC/MIBK Extraction Procedure:

1) 800 ml of sample put in 1-liter separatory funnel.

2) 1.3 ml of 6 M HCl added to bring pH to $\sim$2.2.

3) 4 ml of APDC added (1.2 g commercial APDC dissolved in 25-ml Super-Q and extracted three times with 20 ml MIBK).

4) 20-ml MIBK added; shaken for one mix and allowed to separate for 10 minutes.

5) MIBK layer collected in 100-ml beaker and evaporated to dryness (with heating and gas [N_2 or Ar] bubbling over it).

6) 1-ml distilled HNO_3 added and evaporated to dryness.

7) 1-ml distilled HNO_3 added, heated slightly, and transferred to falcon tube.

8) 1-ml filtered seawater and several portions of Super-Q used to rinse beaker; transferred into falcon tube.

9) All samples and standards are brought to same final weight (usually about 9 g); Cd, N, and Zn measured by PES.

10 Lines to End of Typing Area

PDCA-$HCCl_3$ Procedure (Modifications):

Step 2: Use 0.8 ml 8N distilled HNO_3.

Steps 3 & 4: The PDCA is dissolved in the $CHCl_3$ in a concentration of $\sim$0.15 M. This is a slightly higher concentration of PDCA than was used in the previous procedure. Twenty ml of the PDCA/$CHCl_3$ solution is used.

Selenium is analyzed by direct hydride generation into the plasma.

For Page Numbering

Organism Analysis

Treatment of Samples:

1) Flounder: Weight of whole organism recorded.

Initially, whole flounder pureed in blender (with a little seawater), freeze dried, and two samples taken from each flounder (analysis showed high nickel contamination from the stainless steel blender).

Starting with samples from July 18, whole organism freeze dried, cut up with surgical grade scissors into small pieces, two samples from each flounder taken.

2) Mya: Weight of whole organism recorded.

Initially, whole organism pureed in blender with seawater, freeze dried, and sample taken.

Starting with samples from July 14, whole organism freeze dried and ground with mortar and pestle and sample taken.

3) Littorina: Two whole organisms were freeze dried and combined to get enough sample weight.

4) Zostera: Whole plant was freeze dried.

Initially, whole plant analyzed together. Starting July 14, root and blade analyzed separately.

Digestion Procedure:

All glassware was soap and water washed, acid soaked (1:160 HNO_3 at least overnight) and rinsed with Super-Q water.

1) Dry sample weights were usually between 0.2 and 0.5 g; put into 50-ml round-bottom flasks.

2) 5 ml distilled HNO_3 added; refluxed for 1/2 hour.

3) 5 ml perchloric acid added; refluxed for 1/2 hour.

4) Initially, allowed to evaporate for 1/2 hour. Starting July 13, this was no longer done except for the Zostera samples.

5) Transferred to 25-ml volumetric flasks.

6) 5-ml filtered seawater added (used to rinse round-bottom flask) and brought to volume with Super-Q water (used to rinse round-bottom flask).

7) All four elements measured by PES.

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Long-Term Bioassay

Observations:

1) Flounder: There seemed to be no pattern governing the distribution of the flounder in the tanks. For the first three days of the test, the flounder in Tank #3 (LS3) were very active and stirred the sludge to such an extent that it was difficult to see into the tank. When they calmed down and the visibility increased to allow observation of the sediment surface, the bottom was covered with a nearly homogeneous layer of LS3 and gravel mixture. The only other observation noted concerning the flounder was that those fish in Tank #3 seemed to have ravenous appetites and those in Tank #2 did not eat as much as those in the other three tanks. This could be due solely to the personalities of the individual fish.

2) Mya: The *Mya* were noted to burrow more in the softer, finer sediment of the *Zostera* bed or sludge layer than in the gravel. About half of the clams in each tank were buried; one or two had dug into the gravel.

3) Zostera: The *Zostera* in the DA1 tank (#5) died before those in the other three tanks (July 22 vs. ~July 28). Also, the portion of the plant bed that was in the sludge died faster than that in the sand substrate.

4) Littorina: The Littorina were found most often on the walls of the tanks or in the eelgrass. They congregated in groups of four or more, especially during the day, mostly out of the water. In Tank #7 (L1) there seemed to be one large congregation of about 30 animals that remained high on the back wall of the tank. As the experiment progressed, the snails became less apt to crawl completely out of the tanks, staying closer to the water. For the last weeks, they remained submerged most of the time. Often, an animal had to be removed from inside the overflow pipe.

10 Lines to End of Typing Area

Due to the high mortality of the clams and snails in the LS3 *Zostera* tank (see Mortality Record in the following exhibit), a separate tank was set up to receive the overflow water from this tank. The purpose was to see if the toxic factor was the sludge itself or if something was being leached from the sludge. Eight softshell clams were put into the tank along with a sand substrate. As of August 7, 1978, six of the clams had died. These were subsequently frozen in the event of future analysis.

In addition, two of the clams that died in Tank #6 were autopsied to see if there were any obvious physical abnormalities. The first clam showed nothing; however, the second clam did have a large amount of fine-grain sludge within the mantle and gill. It is possible that physical clogging of the gill membranes may have caused the death, although the clam may also have died while it was partially buried and the silting occurred when the adductor relaxed. Both clams showed no evidence of sludge in the gut.

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Water Quality:

The temperature in the tanks varied as follows:

Tank	°C	s.d.
1	17.0	± 0.9
2	17.0	± 0.9
3	16.7	± 1.0
4	16.7	± 0.9
5	17.4	± 1.1
6	17.7	± 1.0
7	18.0	± 0.9
8	19.4	± 1.4
overflow	20.9	± 1.4
line	15.0	± 0.8

The dissolved oxygen fluctuated with the flow rates and amount of activity in the tanks. By the 5th of July, it was stable at ∿5 ppm in all the tanks, and by July 17, it was stable above 6 ppm. At no point did the D.O. fall below a critical level, i.e., ∿3 ppm, in any of the tanks.

The salinity remained at 31-32 ppt throughout the test.

The pH averaged 7.7 in the flounder tanks, 7.8 in the Zostera tanks (including the overflow tank from LS3), and 7.8 in line water. The DA1 tanks ran slightly higher: 7.8 in the flounder tank (#4) and 7.9 in the Zostera tank (#5).

The ammonia levels in the flounder tanks decreased steadily from a high of ∿800 ppb to less than 200 ppb. The Zostera tank levels decreased over the duration of the test, and by the end was running at less than 100 ppb, or just slightly higher than line water (complete water quality data are given in the exhibit).

10 Lines to End of Typing Area

054-1279-100M For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Exhibit

10 Lines
to End of
Typing Area

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

MORTALITY RECORD

Date	Number	Organism	Tank No.	Sludge
3 July	2	Pseudopleurenectes	1	Control
	1	Littorina	8	Control
5 July	1	Mya	6	LS3
	1	Littorina	6	LS3
6 July	4	Mya	6	LS3 (autopsy)
7 July	1	Mya	6	LS3
	2	Littorina	6	LS3
8 July	1	Mya	6	LS3 (autopsy)
11 July	1	Littorina	5	DA1
12 July	1	Littorina	5	DA1
	3	Littorina	6	LS3
20 July	2	Littorina	6	LS3
	1	Littorina	8	Control
21 July	1	Mya	6	LS3
	1	Mya	overflow tank	LS3
24 July	1	Littorina	6	LS3
	1	Littorina	8	Control
25 July	2	Mya	overflow tank	LS3
26 July	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
27 July	1	Mya	overflow tank	LS3
	1	Littorina	5	DA1
7 August	1	Mya	overflow tank	LS3

For Page Numbering

DATE	Tank	(°C.) Temp.	(ppm) D.O.	(ppt) Salinity	pH	(ppb) NH_3.
3 July	1	16.2	5.5	32	8.0	360
	2	17.1	4.6	32	7.7	868
	3	15.8	5.8	32	7.7	326
	4	15.9	5.3	32	7.7	272
	5	18.3	4.1	31	7.8	476
	6	18.6	3.6	32	7.6	430
	7	17.8	4.7	32	7.7	402
	8	19.4	3.6	31	7.8	606
	line	13.6				
4 July	1	17.5	5.0			
	2	17.1	5.0			
	3	17.0	4.9			
	4	17.3	4.1			
	5	18.8	3.9			
	6	18.8	5.0			
	7	18.8	4.9			
	8	19.6	4.2			
5 July	1	16.1	5.1	31		368
	2	16.2	5.7	31		448
	3	15.6	6.0	31		278
	4	15.7	5.5	31		308
	5	17.4	3.8	31		222
	6	17.5	4.2	31		316
	7	17.1	5.2	31		252
	8	18.2	4.7	31		350
6 July	1	15.6	6.8			
	2	15.6	7.0			
	3	15.5	6.6			
	4	15.7	6.2			
	5	16.7	5.4			
	6	17.5	5.5			326
	7	17.3	6.4			
	8	18.3	5.6			
	line	13.9				66

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
7 July	1	16.3		32		
	2	16.4		32		
	3	16.3		32		
	4	16.6		32		
	5	18.0		32	7.8	
	6	19.0		32	7.7	
	7	18.9		32	7.7	
	8	20.3		32		
	line			32	7.8	
10 July	1	16.7	6.5			
	2	17.6	6.3			
	3	16.1	6.6			
	4	16.4	6.0			
	5	16.8	6.5			
	6	16.5	7.1			
	7	17.6	6.5			
	8	22.6	5.7			
11 July	1	17.4	6.1	31	7.7	
	2	17.4	6.5	31	7.8	
	3	18.3	4.9	31	7.7	
	4	17.5	5.5	31	7.9	
	5	17.7	6.6	31	8.0	
	6	18.2	6.6	31	8.0	
	7	18.4	6.5	31	7.9	
	8	20.4	5.9	31	7.8	
	line	14.8	8.0	31	7.9	
12 July	1	16.8				224
	2	16.7				
	3	16.6				
	4	16.6				226
	5	16.4				
	6	16.6				216
	7	17.8				
	8	20.1				
	line	15.4				80

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
13 July	1	17.2	6.0	31		
	2	17.3	6.1	31		
	3	17.1	5.9	31		
	4	17.2	5.1	31		
	5	17.6	6.4	31		
	6	17.3	6.9	31		
	7	18.6	6.1	31		
	8	20.9	5.8	31		
	overflow	19.8	6.6	31		
	line	14.9	7.6	31		
17 July	1	17.4	6.3	31	7.4/7.5	
	2	18.2	6.0	31	7.7/7.5	338
	3	16.9	6.3	32	7.6	356
	4	16.6	6.1	32	7.7	215
	5	17.0	6.0	32	7.8	
	6	18.2	6.4	32	7.7	
	7	19.2	5.9	32	7.7	
	8	19.0	6.4	32	7.7	
	overflow	22.0		32		
	line	14.0	7.4	32	7.7	
18 July	1	16.5				
	2	17.2				
	3	16.0				
	4	16.2				
	5	16.3				
	6	17.8				
	7	17.5				
	8	20.1				
	overflow	21.3				

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
19 July	1	16.7				250
	2	17.3				308
	3	16.3				258
	4	16.5				272
	5	16.9				100
	6	17.4				104
	7	18.6				113
	8	21.1				112
	overflow	21.0				110
	line	15.3				112
20 July	1	17.0	6.4	32		
	2	16.6	6.7	32		
	3	16.5	6.2	32		
	4	16.6	6.0	32		
	5	17.0	6.7	32		
	6	17.5	6.9	32		
	7	17.7	6.6	32		
	8	19.2	7.1	32		
	overflow	21.8	6.3	32		
	line	15.3	7.4	32		
24 July	1	19.1			7.6	
	2	18.8			7.7	
	3	18.4			7.7	
	4	18.8			7.7	
	5	19.4			7.8	
	6	20.1			7.8	
	7	19.4			7.8	
	8	21.3			7.8	
	overflow	23.7			7.7	
	line	16.1			7.7	

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
25 July	1	16.4	6.5	32		155
	2	16.4	6.4	32		133
	3	16.1	6.1	32		181
	4	16.7	6.1	32		177
	5	17.0	6.9	32		81
	6	18.0	7.3	32		
	7	18.5	6.7	32		
	8	19.1	7.4	32		
	overflow	22.0	6.2	32		95
	line	14.9	7.4	32		57
26 July	1	17.2				
	2	17.0				
	3	16.8				
	4	17.1				
	5	17.4				
	6	17.7				
	7	18.1				
	8	19.6				
	overflow	21.1				
	line	14.7				
27 July	1	17.3				
	2	17.1				
	3	16.8				
	4	17.0				
	5	17.3				
	6	17.4				
	7	17.7				
	8	18.6				
	overflow	20.6				
	line	14.3				

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
31 July	1	15.9	7.4			
	2	15.7	7.4			
	3	15.7	7.1			
	4	15.8	7.1			
	5	16.3	7.9			
	6	16.3	-			
	7	16.3	8.0			
	8	17.7	8.7			
	overflow	18.9	7.3			
	line	15.0	7.9			
1 Aug.	1	15.7	6.8	32		157
	2	15.6	7.0	32		
	3	15.4	6.4	32		
	4	15.7	6.6	32		
	5	15.7	7.5	32		
	6	16.0	-	-		
	7	16.6	7.6	32		
	8	16.4	8.0	32		67
	overflow	18.6	7.4	32		65
	line	14.1	7.6	32		49
2 Aug.	1	16.2	6.9		7.9	
	2	16.1	6.5		7.9	129
	3	15.9	5.9		7.8	165
	4	16.0	5.9		7.8	217
	5	15.9	7.3		8.1	72
	6	-	-		-	-
	7	16.3	7.2		8.0	60
	8	16.7	7.8		8.0	
	overflow	18.2	7.1		8.0	
	line	14.6	7.8		7.9	50

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
3 Aug.	1	16.0				
	2	16.1				
	3	15.8				
	4	16.0				
	5	15.9				
	7	16.8				
	8	17.4				
	overflow	19.4				
4 Aug.	1	17.3				
	2	17.0				
	3	17.0				
	4	17.3				
	5	17.3				
	7	17.5				
	8	18.7				
	overflow	21.0				
	line	14.9				
8 Aug.	1	18.3	6.4	31		
	2	18.4	6.3	31		
	3	17.8	6.0	31		
	4	18.0	6.2	31		
	5	18.1	6.9	31		
	7	18.6	6.7	31		
	8	19.9	7.0	31		
	overflow	22.2	6.6	31		
	line	16.2	7.2			

DATE	Tank	Temp.	D.O.	Salinity	pH	NH_3
9 Aug.	1	18.4			7.7	
	2	18.4			7.7	
	3	18.2			7.6	
	4	18.4			7.6	
	5	20.0			7.8	
	7	18.6			7.8	
	8	19.6			7.8	
	overflow	21.7			7.8	
	line	16.3			7.7	
10 Aug.	1	18.9				
	2	18.4				
	3	18.6				
	4	18.9				
	5	19.1				
	7	19.9				
	8	20.0				
	overflow	21.9				
	line	16.6				
11 Aug.	1	18.0	6.9	32		
	2	17.9	6.7	32		
	3	17.9	6.6	32		
	4	18.1	6.6	32		
	5	18.4	7.0	32		
	7	19.2	6.9	32		
	8	19.7	7.2	32		
	overflow	21.3	7.3	32		
	line	15.8	7.3	32		

Is this another Progress Report?

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

Summary of Trace Element Measurement Results

A. WATER SAMPLES

1) CD levels in Tanks #2 and #6 were initially higher than expected, indicating the leaching of Cd, perhaps from the FGD layers. By 6/6/78, Cd concentrations were normal.

2) Ni levels remained below those that should have been present for Tanks #2, 3, 6, and 7 throughout the test. Apparently, Ni precipitated or was taken up by one or more of the solid surfaces in the tanks.

3) The smaller tanks usually contained higher concentrations of all four elements than did the flounder tanks. This pattern was likely due to the difficulties encountered in maintaining the desired turnover water flow rates in the small tanks.

B. TISSUE SAMPLES

1) Nickel data for flounder and Mya samples taken before 7/28 should be discounted, since some of them may reflect contamination of the samples during homogenization in a stainless steel blender.

2) Based on the data of 7/28-8/17, the following trends in the accumulation of the four elements are evident:

   a) Flounder do not seem to be accumulating significant levels of any of the elements.

   b) Mya in Tanks #6 and 7 accumulated Se, Cd, and Ni. The extent of Se accumulation cannot be assessed given the lack of detectable levels of Se in baseline and control populations. Cd levels are an order of magnitude higher in the tissues of Mya in Tanks #6 and 7 than in those from Tanks #4 and 8 (control).

   c) Littorina also accumulated high levels of Se, Cd, and Ni in Tanks #6 and 7.

   d) Zostera data vary considerably and were likely affected by FGD attached to the roots and occasionally to the leaves.

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 7/3/78 (Duplicates analyzed)

Tank No.	Concentration (µg/ℓ)			
	Zn	Ni	Cd	Se
1	2 3	<1 <1	1 <1	<5 <5
2	17 18	7 6	12 12	82 86
3	31 41	9 18	32 30	58 59
4	1 4	<1 <1	<1 1	<5 <5
5	1 2	1 1	7 7	5 5
6	45 37	10 8	27 33	75 80
7	9 6	7 6	8 6	56 66
8	2 2	<1 1	1 1	<5 <5

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 7/7/78

Tank No.	Concentration (µg/ℓ)			
	Zn	Ni	Cd	Se
1	4	<1	<1	<5
2	28	15	5	120
3	33	10	14	90
4	4	<1	<1	<5
5	2	<1	<1	<5
6	44	14	22	116
7	12	9	3	118
8	4	3	<1	<5

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8 1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 7/18/78 (Duplicates analyzed)

Tank No.	Concentration (μg/ℓ)			
	Zn	Ni	Cd	Se
1	4	1	0.2	<2
	4	1	0.3	<2
2	6	6	3.0	51
	13	10	3.9	61
3	17	7	8.1	45
	22	8	8.6	48
4	5	1	0.5	<2
	4	<1	0.6	<2
5	6	1	0.2	<2
	4	<1	0.3	<2
6	30	11	33	89
	33	11	31	95
7	14	10	6.2	90
	14	11	6.1	102
8	4	<1	0.4	<2
	3	<1	0.6	<2

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8 1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 7/28/78

Tank No.	Concentration (μg/ℓ)			
	Zn	Ni	Cd	Se
1	5	1	<1	<5
2	15	10	5	108
3	24	5	13	81
4	6	1	<1	<5
5	14	1	2	<5
6	28	7	15	97
7	17	13	6	129
8	5	1	1	<5

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 8/10/78 (Duplicates analyzed)

Tank No.	Concentration (µg/ℓ)			
	Zn	Ni	Cd	Se
1	5	1	<1	<5
	4	1	<1	<5
2	17	9	4	124
	15	7	4	101
3	21	6	14	93
	22	5	13	106
4	8	1	<1	<5
	6	1	<1	<5
5	7	1	<1	<5
	11	<1	2	<5
6	28	14	9	111
	31	13	10	99
7	17	16	5	112
	14	13	3	118
8	9	<1	1	<5
	8	<1	<1	<5

10 Lines to End of Typing Area

For Page Numbering

USE THIS SHEET FOR REPORT TYPING 8-1/2 x 11

TOP

RESULTS OF TRACE ELEMENT MEASUREMENTS
F.G.D. Long-Term Bioassay

Samples : Test Tank Seawater
Sampling Date : 8/17/78 (Duplicates analyzed)

Tank No.	Concentration (μg/ℓ)			
	Zn	Ni	Cd	Se
1	6	<1	<1	<5
	4	<1	<1	<5
2	12	9	3	95
	13	4	4	108
3	22	8	12	87
	30	12	14	83
4	4	<1	<1	<5
	3	<1	<1	<5
5	3	<1	<1	<5
	3	<1	<1	<5
6	All organisms dead - flow off			
7	12	15	3	139
	17	13	5	123
8	5	<1	<1	<5
	3	<1	<1	<5

10 Lines to End of Typing Area

For Page Numbering

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/3/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	314	192	40	<0.2	< 8
	2	526	88	10	<0.2	< 5
	3	566	122	< 2	<0.2	< 5
	4	555	89	9	<0.2	< 5
Mya	8	481	85	36	2.1	< 5
	7	395	138	3.0	2.0	< 7
	6	668	122	16	4.0	17
	5	416	129	3.3	1.4	< 6
Littorina	8	67	69	< 4	< 1	<34
	7	133	89	11	0.9	16
	6	117	188	< 2	0.6	<22
	5	106	64	< 2	< 1	<23
Zostera	8	374	168	1.2	4.2	< 7
	7	565	147	31	2.5	< 5
	6	1859	59	11	4.8	< 1
	5	156	185	< 2	<0.8	<17

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/5/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	490	132	8	0.5	<5
	2	505	140	7	0.4	<5
	3	508	125	6	0.4	<5
	4	482	129	10	0.4	<5
Mya	8	485	84	6	0.8	5
	7	487	112	23	5.7	8.5
	6	494.	78	12	10.0	14
	5	504	130	24	1.6	<5
Littorina	8	96	165	8	2.5	<25
	7	43	144	23	3.6	<45
	6	100	179	158	8.0	<25
	5	101	170	23	3.0	<25
Zostera	8	228	36	8	3.2	<10
	7	208	133	17	4.6	<12
	6	164	104	138	10.0	<15
	5	180	115	27	0.3	<15

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/5/78 (Duplicate samples)

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	192	94	17	0.6	<13
	2	192	158	9	0.8	<13
	3	330	166	5	0.4	< 8
	4	225	156	8	1.0	<11
Mya	8	214	114	21	1.0	<12
	7	390	119	25	4.2	< 6
	6	246	226	19	14	28
	5	310	113	55	0.8	< 8
Littorina	8	74	69	< 3	<.2	<35
	7	96	51	< 5	<1	<25
	6	161	137	3	12	31
	5	97	140	114	<.2	<25
Zostera	8	159(L)	225	6	4.4	<15
		94(R)	122	< 2	3.8	<30
	7	338(L)	240	27	3.5	12
		335(R)	123	21	3.4	16
	6	301(L)	448	37	31	33
		61(R)	2000(?)	234	142	380
	5	225(L)	156	2	3.2	<11
		373(R)	132	9	1.9	< 7

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/7/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	276	148	13	2.4	< 9
	2	288	89	3.4	1.0	< 9
	3	305	130	17	0.6	<10
	4	265	107	18	0.8	<11
Mya	8	158	130	40	1.4	<15
	7	254	49	13	3.1	<10
	6	262	112	15	35	46
	5	230	182	9	0.7	<10
Littorina	8	97	74	2.5	6.8	<25
	7	107	104	17	4.9	<25
	6	100	147	20	10	<25
	5	25	64	54	3.9	<100
Zostera	8	611(L)	146	5	3.5	< 5
		343(R)	83	8	2.9	< 8
	7	231(L)	135	22	5.5	33
		209(R)	121	10	4.1	21
	6	348(L)	122	21	17	46
		221(R)	74	9	6.9	37
	5	163(L)	110	3	2.2	<15
		166(R)	73	29	0.6	<15

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/14/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	281	83	<2	0.6	<10
	2	396	94	<2	0.2	< 8
	3	328	139	<1	0.4	< 8
	4	343	115	<2	<0.1	< 8
Mya	8	315	65	0.7	1.0	< 8
	7	181	118	49	8.5	<15
	6	222	1284	5.5	18	32
	5	202	94	1.9	<0.1	<12
Littorina	8	87	105	4.0	<0.1	<30
	7	78	271	37	11	<30
	6	77	115	2.2	13	<30
	5	27	495	31	16	<100
Zostera	8	338(L)	126	5.1	4.4	<6
		447(R)	54	1.7	1.6	<8
	7	126(L)	104	18	4.5	<20
		593(R)	53	12	2.2	< 5
	6	744(L)	148	14	15	4
		202(R)	153	18	2.3	45
	5	118(L)	92	14	2.5	<25
		239(R)	117	7.6	1.6	<10

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/18/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	355	158	7	1.4	<12
	2	278	220	5	1.6	<17
	3	358	156	6	1.5	19
	4	302	298	4	2.2	<15
Mya	8	162	102	31	3.8	30
	7	370	116	7	12	25
	6	224	152	31	46	74
	5	288	102	4	1.5	<15
Littorina	8	137	89	16	6.8	<38
	7	125	83	40	50	720
	6	91	200	120	35	36
	5	117	170	71	1.7	<32
Zostera	8	323(L)	44	15	1.9	15
		583(R)	72	8	.8	< 8
	7	492(L)	157	45	7.4	86
		398(R)	175	50	8.3	103
	6	491(L)	224	32	29	68
		88(R)	122	20	8.7	<50
	5	139(L)	224	7	34	<32
		291(R)	146	21	1.8	<15

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/18/78 (Duplicate samples)

Organism	Tank #	Sample Wt. (mg)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	470	117	13	.7	< 8
	2	430	102	5.4	1.2	<10
	3	343	155	3.6	2.2	<12
	4	472	140	< .2	.9	< 8
Mya	8	246	84	19	3.5	<16
	7	247	150	20	16	25
	6	308	138	6.1	30	47
	5	246	126	<.7	3.4	<16
Littorina	8	98	211	53	14	<38
	7	154	173	19	12	96
	6	94	246	33	44	28
	5	101	153	33	18	<38
Zostera	8	240(L)	193	26	6.0	<16
		95(R)	222	48	15	<40
	7	473(L)	184	44	6.8	39
		447(R)	152	36	6.7	48
	6	417(L)	239	15	25	31
		393(R)	253	17	27	39
	5	371(L)	124	2.6	7.8	<10
		633(R)	137	10	7.1	< 6

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/21/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	370	145	8	1.5	<8
	2	364	173	8	2.3	<8
	3	374	174	12	1.6	<9
	4	458	135	1.8	1.5	<6
Mya	8	284	112	9	2.4	<10
	7	295	108	13	14	24
	6	354	110	8	30	42
	5	488	77	6	2.7	6
Littorina	8	100	98	<2	3	<25
	7	290	191	33	7	36
	6	195	117	8	33	40
	5	156	117	9	6	<18
Zostera	8	122 (R)	110	4	5	<24
		147 (L)	155	7	6	<20
	7	330 (R)	153	35	8	47
		286 (L)	163	38	9	72
	6	59 (R)	122	99	6	<49
		251 (L)	229	19	12	39
	5	119 (R)	100	15	35	<24
		96 (L)	58	17	63	<30

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 7/28/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	295	109	<2	<1	<9
	2	150	166	<2	1.3	24
	3	282	158	8	3.0	<9
	4	332	114	<2	1.3	<7
Mya	8	176	110	1.1	3.2	<14
	7	234	137	5.1	18	40
	6					
	5	238	113	5.4	2.5	<10
Littorina	8	100	133	10.3	<3	<20
	7	173	127	15	8.2	49
	6					
	5	141	155	8.5	<2	<17
Zostera	8					
	7					
	6					
	5					

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 8/10/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	296	80	1.8	<0.4	<11
	2	444	151	1.9	0.4	20
	3	318	186	5.8	0.4	28
	4	492	118	1.6	0.3	<5
Mya	8	394	104	5.6	0.8	<8
	7	393	127	8.7	19	46
	6					
	5	299	87	2.2	0.4	<11
Littorina	8	314	115	5.1	0.9	<10
	7	152	152	17	3.4	44
	6					
	5	198	122	5.7	0.8	<10
Zostera	8					
	7					
	6					
	5					

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 8/10/78 (Duplicate samples)

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	496	94	1.0	<0.2	<7
	2	442	207	4.0	1.2	10
	3	506	120	1.2	0.3	<6
	4	278	145	1.3	<0.3	<12
Mya	8	393	88	3.5	0.9	<10
	7	268	92	10.1	20	14
	6					
	5	323	105	4.1	1.0	<8
Littorina	8	137	150	9.1	0.7	<20
	7	286	125	13.1	7.4	15
	6					
	5	215	109	7.1	3.4	<14
Zostera	8					
	7					
	6					
	5					

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 8/17/78

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	463	124	1.5	<0.6	<5
	2	437	137	1.4	3.1	8
	3	567	119	1.6	1.5	6
	4	378	109	1.0	<0.8	<6
Mya	8	307	100	6.1	1.3	<8
	7	398	89	10.2	25	31
	6					
	5	336	91	4.1	1.0	<7
Littorina	8	167	134	4.4	2.0	<14
	7	185	127	12.	14.	33
	6					
	5	230	100	3.8	2.8	<10
Zostera	8					
	7					
	6					
	5					

SAMPLES : TISSUES OF TEST ORGANISMS
SAMPLING DATE : 8/17/78 (Duplicate samples)

Organism	Tank #	Sample Wt. (mg.)	Trace Element Concentration (µg/g dry wt.)			
			Zn	Ni	Cd	Se
Flounder	1	420	119	2.0	0.8	<11
	2	436	122	1.5	1.6	<11
	3	421	100	1.1	0.7	<11
	4	423	110	1.1	<0.6	<11
Mya	8	405	97	4.4	1.7	<11
	7	389	115	12.	28.	35
	6					
	5	333	63	2.4	1.5	<14
Littorina	8	229	112	5.0	2.3	<22
	7	257	119	15.	11.	29
	6					
	5	210	98	7.7	1.5	<22
Zostera	8					
	7					
	6					
	5					